T NO. DOT-TSC-NHTSA-78-47   HS-803-722

AN ASSESSMENT OF THE POTENTIAL IMPACT OF COMBUSTION RESEARCH ON INTERNAL COMBUSTION ENGINE EMISSION AND FUEL CONSUMPTION

J.L. Kerrebrock
C.E. Kolb

AERODYNE RESEARCH, INC.
Bedford Research Park, Crosby Drive
Bedford MA   01730

JANUARY 1979

FINAL REPORT

Prepared for

HE
155
.A34
no
DOT-
TSC-
NHTSA
78-47

1. Report No. HS-803-722	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle AN ASSESSMENT OF THE POTENTIAL IMPACT OF COMBUSTION RESEARCH ON INTERNAL COMBUSTION ENGINE EMISSIONS AND FUEL CONSUMPTION		5. Report Date January 1979
		6. Performing Organization Code
7. Author's) J.L. Kerrebrock & C.E. Kolb		8. Performing Organization Report No. ARI-RR-131 DOT-TSC-NHTSA-78-47
9. Performing Organization Name and Address Aerodyne Research, Inc.* Bedford Research Park, Crosby Drive Bedford MA 01730		10. Work Unit No. (TRAIS) HS-927/R9404
		11. Contract or Grant No. DOT-TSC-1487
12. Sponsoring Agency Name and Address U.S. Department of Transportation National Highway Traffic Safety Administration Office of Research and Development Washington DC 20590		13. Type of Report and Period Covered Final Report Dec 1977 to April 1978
		14. Sponsoring Agency Code
15. Supplementary Notes U.S. Department of Transportation Research and Special Programs Administration *Under Contract to: Transportation Systems Center Kendall Square, Cambridge MA 02142		

16. Abstract

A review of the present level of understanding of the basic thermodynamic, fluid dymanic, and chemical kinetic processes which affect the fuel economy and levels of pollutant exhaust products of Diesel, Stratified Charge, and Spark Ignition engines is presented. Key areas are identified where insufficient understanding currently prevents the rational development of internal combustion engines with improved performance. A research plan designed to gather the needed data is presented.

17. Key Words Automotive emissions, Automotive fuel economy, spark ignition engine emissions, Stratified charge engine emissions, Combustion efficiency, Fluid mechanics and Chemical kinetics of Internal Combustion engines.	18. Distribution Statement DOCUMENT IS AVAILABLE TO THE PUBLIC THROUGH THE NATIONAL TECHNICAL INFORMATION SERVICE, SPRINGFIELD, VIRGINIA 22161		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 102	22. Price

Form DOT F 1700.7 (8-72)   Reproduction of completed page authorized

PREFACE

The purpose of this report is to review the present levels of understanding of the basic theromodynamic, fluid dynamic, and chemical kinetic processes which affect the fuel economy and exhaust pollutant levels in Diesel, Statified charge, and Spark Ignition engines for Light Duty Vehicles. Key areas where the levels of understanding are currently insufficient to allow the rational development of improved internal combustion engines are identified, and a research plan designed to gather the needed data is presented.

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in²	square inches	6.5	square centimeters	cm²
ft²	square feet	0.09	square meters	m²
yd²	square yards	0.8	square meters	m²
mi²	square miles	2.6	square kilometers	km²
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft³	cubic feet	0.03	cubic meters	m³
yd³	cubic yards	0.76	cubic meters	m³
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm²	square centimeters	0.16	square inches	in²
m²	square meters	1.2	square yards	yd²
km²	square kilometers	0.4	square miles	mi²
ha	hectares (10,000 m²)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m³	cubic meters	35	cubic feet	ft³
m³	cubic meters	1.3	cubic yards	yd³
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

iv

CONTENTS

v

CONTENTS (CONTINUED)

CONTENTS (CONTINUED)

LIST OF TABLES

1. INTRODUCTION

The conservation of petroleum resources by enhancing the fuel economy of light-duty vehicles is an important national goal. The "Energy Policy and Conservation Act" of 1975 established fleet-averaged passenger car fuel economy standards for 1978, 1979, 1980, and 1985, and gave the Secretary of the Department of Transportation (DOT) the responsibility to set standards for 1981 - 1984. These standards, based on values measured by the manufacturers during Environmental Protection Agency (EPA) certification for emission standards are shown in Table 1-1.

However, at the same time this very significant gain in pre-1978 fleet-averaged fuel economy is being achieved, major reductions in the EPA regulated automobile emissions (nitrogen oxides, carbon monoxide, hydrocarbons) are mandated by the 1977 amendments to the "Clean Air Act." Furthermore, potential changes in engine types driven by fuel economy requirements may force the EPA to institute regulations controlling various classes of hydrocarbon emissions which are not now controlled. Thus, gains in fuel economy cannot be achieved at the expense of air quality, and modifications in engines and drive trains must be compatible with tightening exhaust emissions standards.

The purpose of this document is to report on the development of an assessment of the potential gains is fuel consumption and pollutant emissions which may be realized from research on internal combustion engines. All reciprocating engines will be considered, but the major emphasis will be placed on compression ignition and stratified charge spark ignition engines because they seem to offer new possibilities which have not been exploited as fully as has the homogeneous spark ignition engine.

In this assessment, we will first review the major factors which control the fuel consumption and pollutant emissions and indicate in a general way, how these factors interact for each of the major engine types. We will then discuss in a similar way the competitive position of the diesel and stratified charge engines relative to the carburated (homogeneous) spark ignition engine. It appears that

TABLE 1-1   AVERAGE PASSENGER CAR FUEL ECONOMY STANDARDS

Year	Avg. MPG
1978	18.0
1979	19.0
1980	20.0
1981	22.0
1982	24.0
1983	26.0
1984	27.0
1985	27.5

the heterogeneous combustion piston engine program could benefit from a comprehensive review and application of the extensive research done on aircraft gas turbine combustion systems, and this interface will also be discussed.

On the basis of this general outline, we will then indicate in more detail the areas which appear to offer substantial returns for research investment, either in reduced fuel consumption, reduced emissions, or both.

A final note is in order concerning the difference between emissions and fuel consumption as subjects for research and development. The science and engineering of automotive emissions reduction has been the subject of much research, development, and publication in recent years as a result of the new requirements imposed by emissions regulations starting in 1968. While much progress has been made, there is still work to be done in establishing the fundamentals. In contrast, research on fuel economy has been pursued for a century, and the fundamentals are clearly set out in classic texts, such as those by Lichty[1] and Taylor.[2] Improvements in fuel consumption will probably come from refinements of design and from different compromises between performance and fuel economy driven by the more stringent fuel consumption criteria of the future, rather than from new fundamental concepts. Thus, while the sections of this report dealing with emissions will contain numerous references to the current literature, those dealing with fuel consumption will not. It would be presumptuous to attempt to improve on Refs. (1) and (2) in this regard. Our aim, here, is to present in compact form that part of the knowledge which is most relevant to the present problem.

2. FACTORS WHICH CONTROL FUEL CONSUMPTION

The fuel consumption of a piston engine in automotive use is influenced by many factors in addition to the basic parameters which characterize its thermodynamical, mechanical and fluidmechanical behavior. Such factors as the power transmission and the use cycle, including warmup and maintenance throughout the life of the engine, play almost as large a role as design parameters such as compression ratio and displacement, so that any systematic optimization of engine design for maximum fuel economy consistent with acceptable emissions must consider these aspects of the overall problem. Some of these aspects are included in the current EPA mileage rating system for automobiles but their inadequacy can be judged from the fact that fuel consumption, in practice, usually exceeds the EPA estimates. It follows that a necessary step toward rationalization of engine designs is the development of a methodology for predicting what fuel consumption an engine will have in average use. This deserves substantial effort and some possible approaches to the question will be outlined below.

Supposing for the moment that a method for evaluating engines exists, we can ask what parameters characterize the design and, hence, should be treated as variables in the process of optimization. The tendency in the past has been to deal with specific engine designs, such as spark ignition gasoline engines, Diesel engines, and more recently stratified charge engines. But, it seems now that there is a near continuum of such designs overlapping each other in regard to their fundamental processes. So for the present discussion the engine will rather be characterized by the thermodynamic, fluidmechanical and operational results of the design choices.

In these terms, the factors controlling the fuel consumption are:

1. The compression ratio,

2. The heat addition schedule,

3. The method of load variation,

4. The working fluid composition,

5. Sizing and piston speed, and

6. Power transmission characteristics.

The effect of each of these on fuel consumption will be discussed in this section, while their impact on emissions will be addressed in Section 3.

2.1 COMPRESSION RATIO

Given some ideal means for adding heat to the working fluid at minimum volume, the optimum compression ratio would be determined by a balance between the improved thermodynamic efficiency resulting from increased compression ratio and the reduced mechanical efficiency and greater weight which the higher compression pressures entail. Both power per unit of displacement and indicated thermal efficiency increase continuously with compression ratio in this ideal case. But, the increased bearing sizes, stronger pistons and increased number of rings, and greater structural rigidity lead to both more friction and more weight. With current materials and design techniques, for the optimum compression ratio of minimum fuel consumption from this stand-point, seems to be in the range of 12 to 17.[3] This value is, of course, somewhat sensitive to design sophistication and materials and could change with intensive development.

At present, the actual choice of compression ratio is constrained by other factors. In the homogeneous carburated spark ignition engine it is limited by knock and/or by the NO_x level in the exhaust which increases with increasing compression ratio unless peak combustion temperature is lowered by some means, such as, exhaust gas recirculation. During the late 1950's, U.S. production engines attained compression ratios of 10 or slightly higher. Few are above 8 or 8.5, now. It should be possible to approach the knock limited values in stratified charge engines if the NO_x level can be controlled by tailoring of the mixture ratio to avoid NO_x producing conditions. This could result in as much as 10% reduction in fuel consumption.[1] In the Diesel engine, a lower limit to compression ratio is set by fuel ignition requirements which is above the optimum for automotive use, one result being that Diesels produce less power per unit displacement and per unit of engine mass than spark ignition engines. The cold starting

-5-

requirement is partially circumvented by means of glow plugs, but smooth low speed performance still requires compression ratios of the order of 17 in direct injection engines. Prechamber engines require higher compression ratios to offset the heat loss which the air suffers in passing into the antechamber from the main combustion chamber.

True optimization for fuel consumption should be possible by combining fuel injection into the cylinder with spark ignition as in the Texaco Combustion Process, provided composition can be controlled adequately to yield efficient combustion and sufficiently low emissions. To date, these requirements have not been met. Whether they can be met with further research and development will be discussed in Section 4.

2.2 HEAT ADDITION SCHEDULE

Ideally, the heat addition or more precisely, the pressure rise associated with heat addition, should occur at minimum volume in order to maximize the efficiency. In practice, the heat addition is always spread over an appreciable range of crank angle by the finite fuel injection rate in the Diesel and by the combustion rate in the spark ignition engine. Thus, in each the combustion process must be initiated well before top dead center, the rough rule being that half the pressure rise associated with combustion should occur before top dead center and half after.[1] Heat loss considerations modify this conclusion somewhat since the effective heat loss for fuel injected and burned early in the cycle is larger than that for fuel burned later when the piston is moving more rapidly.[2]

In throttled carburated spark ignition engines running at high speeds and low manifold pressures, a common situation, a large spark advance is required because of the low flame speed in the relatively low pressure charge, which is also diluted with clearance gases. This contributes significantly to the poor fuel economy of the gasoline engine under light loads. The Diesel does not suffer from this problem because its air charge pressure is maintained at partial load and because the reaction time for the injected fuel is lower compared to the available time than at full load.[2]

-6-

Thus all heat addition can take place shortly after top dead center where it is most efficient, and the Diesel has excellent part load fuel economy.

Stratified charge engines offer the same possibility for optimal heat addition timing as the Diesel provided they use direct injection into the combustion space. But the conditions are more stringent because the charge must be ignited by a spark plug rather than on contact with the air. In this case, heat addition rates can be convectively limited. If carburated they still offer an advantage in that the flame speed in the richer zone can be higher because of less dilution with exhaust gases, making a shorter spark advance possible.[3]

A further consideration in choosing the heat addition schedule is noise. Diesels are noisy compared to spark ignition engines at part load conditions. This is because they operate with high cylinder pressures and with rapid combustion pressure rise at part load while the spark ignition engine has very low pressures and a gentle pressure rise. It can be expected that a stratified charge engine will be noisy at part load if optimized for minimum fuel consumption, and hence unthrottled.

2.3 LOAD VARIATION

In normal automotive applications, engines are required to operate over a wide range of load at any given speed. This is not a firm requirement, as will be discussed in Subsection 2.6, but it is accepted practice at present. All engines suffer some loss in efficiency because of the increased friction power which results from the engine turning faster than it would to produce the same power at full throttle. The air pumping loss, in particular, which is usually included in friction losses increases more than proportionately with speed. Since the engine friction can be as much as 40% of the total power at road loads, substantial inefficiencies are associated with the requirement for quick reserve power at fixed engine speed. This point will be discussed further in Subsection 2.6.

Carburated spark ignition engines suffer further losses at part load due to throttling. The air is dropped in pressure across the throttle, and must be pumped back up to atmospheric pressure before discharge in the exhaust. The Diesel engine doe not suffer from this penalty since it operates unthrottled. Most Diesel fuel injection systems meet changing load requirements at a given speed by varying the period of fuel injection, lengthening it for high load operation. This leads to fuel injection late in the cycle at high loads and, hence, to incomplete combustion and smoking. If the high load condition were met by increasing fuel injection rate near top center, the higher pressure rise would result in increased structural loads

Depending on whether load reductions are accepted by throttling its airflow or by increased stratification at constant manifold pressure, the stratified charge engine can exhibit part load characteristics similar to either the diesel or the homogeneous spark ignition engine. The Honda CVCC[4] engine is throttled while the experimental Texaco Controlled Combustion System[5] (TCCS) and Mitsubishi Combustion System (MCS)[6] would permit unthrottled operation.

2.4 WORKING FLUID COMPOSITION

Variations in the specific heat of the working fluid with temperature and with composition lead to large effects on the efficiency of piston engine cycles. For a Diesel cycle with compression ratio of 18, the theoretical fuel-air cycle efficiency varies from 0.42 at 100% of theoretical air to 0.53 at 300% of theoretical air while for the Otto cycle at a compression ratio of 8, the efficiency goes from 0.39 with 100% of theoretical air to 0.56 for the air cycle.[1] There are two reasons for these changes. First, a larger amount of energy is required to affect a given change of temperature, and, hence, of pressure in combustion products than in air because of the larger specific heat of the polyatomic gases, such as, H_2O and CO_2. The second is that a lower maximum temperature is reached as the mixture is leaned from stoichiometric, emphasizing the first effect.

No real engine receives the full benefit of this effect since in the Diesel and stratified charge engines, the air that does combust the fuel does so nearly stoichiometrically, but it expands and does work by compressing the unburned air so its peak temperature is lower than it would be for a uniform mixture. This effect

contributes substantially to the peak load fuel economy of the Diesel and the stratified charge engine with in-cylinder fuel injection should show a similar benefit.

Some improvement in fuel economy can be achieved by diluting the near-stoichiometric fuel air mixture of a carburated spark ignition engine with an inert gas. This lowers the peak temperature reducing the specific heat of the working fluids. It also reduces the power for a given displacement. Ideally, an inert gas of low molar specific heat, e.g., argon, would be desirable. In practice, exhaust gases are recirculated, mainly to reduce NO_x production. Since these gases contain a good deal of CO_2 and H_2O which have large specific heats, they are less than ideal for the purpose, but a small increase in fuel economy can, nevertheless, result.

2.5 SIZING AND PISTON SPEED

There are two choices to be made here, namely, the level of vehicle performance, which is determined by the excess of power available over that required for steady state operation of the vehicle, and the level of engine performance as measured by power per unit displacement. Other factors being equal, fuel economy is deteriorated by providing for greater performance in either sense. To achieve increased vehicle performance, the engine must have larger friction and pumping losses in normal operation since its fractional load at these conditions is reduced. But, this is not determined solely by engine displacement since a large engine turning slowly can exhibit smaller friction losses than a small, rapidly turning one of the same maximum output. The greater weight of the larger displacement engine will impose a performance penalty which must be weighed against the fuel consumption penalty that results from the operation of the smaller engine at high piston speed.

This latter penalty stems from at least three sources. Operation at high piston speeds implies high gas velocities in the engine ports, hence, larger pumping losses which increase fuel consumption. The pressure loss varies roughly, as speed squared for fixed geometry. Finally, as the piston speed

increases, dynamic effects in the intake and exhaust processes become important so that to attain high volumetric efficiencies it is necessary to introduce overlap between the exhaust valve closing and the intake valve opening. This overlap, if chosen for high volumetric efficiency at high engine speeds, results in a reduction of both volumetric efficiency and effective compression ratio at low speeds. A significant increase in fuel consumption is thus, associated with high engine performance.

Supercharging is another option. It allows an increase in output per unit displacement without the penalties of high piston speed. Geared positive displace-ment superchargers, such as, those used on some aircraft engines and Diesels give a nearly uniform power increase across the whole speed range. Geared or exhaust turbine-driven turbo superchargers on the other hand, increase power much more at high engine speeds or high engine airflows in the latter case. The exhaust turbocharger, in particular, offers the possibility of high peak output and good vehicle performance without the fuel consumption penalties at light load conditions which are associated with large displacement or high piston speed, provided the compression ratio at low power is not limited by knock at maximum power conditions.[2] If the engine operates at fixed compression ratio at all loads, there is a fuel consumption penalty due to the reduction in compression ratio required to avoid detonation as the supercharge is increased. But by using valve control, for example, an engine could be operated with a larger compression ratio at low pressure than at the supercharged condition.

2.6 POWER TRANSMISSION CHARACTERISTICS

The ideal automotive transmission would, for any desired power to the drive wheels, hold the engine at the operating condition that gives best fuel economy, and also adjust the operating point instantly in response to changes in power demand. Conventional automatic transmissions approximate to this ideal by means of one or more gear ratio changes combined with hydrodynamic torque conversion, so that the engine runs slowly when the power demand is small and faster for acceleration or hill climbing. But the engine, nevertheless, operates most of the time at very low manifold pressures with larger throttling and friction losses than are necessary in

principle. Typically, the specific fuel consumption is about twice as large at road load conditions as at full throttle for road load power so that large gains in fuel consumption are possible in principle by optimizing the transmission.

The problems are formidable, however. When the power demand is small, the engine must run very slowly. To meet a sudden demand for increase in power, the engine speed would have to be increased rapidly, and conversely a reduction in demand would imply a sudden decrease in engine speed. These requirements indicate a higher level of sophistication in the engine and transmission controls than has been evident to date, but they represent a large potential for exploitation of the rapidly developing digital control technology.

3. FACTORS WHICH CONTROL EMISSIONS

3.1 BACKGROUND ON REGULATED EMISSIONS

The EPA is currently mandated to regulate three classes of light-duty vehicle exhaust emissions. These are: oxides of nitrogen (primarily NO and NO_2) which are measured as equivalent NO_2 and generally designated NO_x; carbon monoxide (CO); and unburned or partially burned hydrocarbons (HC). Table 3-1 shows currently scheduled light-duty vehicle exhaust standards for each of the pollutants, as mandated by the 1977 amendments to the Clean Air Act. The EPA may allow partial waiver of the post-1980 NO_x standard (not to exceed 1.5 g/mile) in cases where a manufacturer utilizes an innovative power train technology, innovative emission control system or Diesel engine technology. Partial easing of the 1981 and 1982 CO and NO_x standards may also be allowed under certain conditions.

TABLE   3-1   FEDERAL LIGHT-DUTY VEHICLE EXHAUST EMISSION STANDARDS

Pollutant	1977	1978	1979	1980	1981	1982	1983	1984
HC	1.5	1.5	1.5	0.41	0.41	0.41	0.41	0.41
CO	15.0	15.0	15.0	7.0	3.4	3.4	3.4	3.4
NO_x	2.0	2.0	2.0	1.0	1.0	1.0	1.0	1.0

The regulation of automotive emissions of NO_x, CO, and HC is based on sound scientific reasoning. Both CO and NO_x are extremely toxic gases in their own right, and levels currently found in relatively undiluted automotive exhausts can lead to loss of consciousness and death. Furthermore, chronic exposure to sublethal doses of CO

is suspected of playing a key role in the development of cardiovascular diseases, since the continued formation of carboxy hemoglobin reduces the oxygenation potential of red blood cells, thus increasing strains on the heart and arterial system.

However, the major reason for the regulation of exhaust NO_x, CO and HC is the role each plays, even after dilution in ambient air, in the development of photo-chemical smog. The major detrimental characteristic of photochemical smog is its high concentrations of oxidant species which produce eye and respiratory irritation in humans and animals as well as extensive damage to plants and materials.[7] These oxidant species include ozone (O_3), peroxyacetylnitrates (PAN), organic peroxy radicals (ROO), hydroperoxy radicals (HOO), and hydroxyl radicals (OH), as well as the NO_x species themselves.

The involvement of each of the regulated pollutants in photochemical smog formation is well documented.[7,8,9,10] NO_x provides the primary formation mechanism of ozone via photolysis of NO_2:

$$NO_2 + h\nu \ (\lambda < 4300\overset{o}{A}) \longrightarrow NO + O \qquad , \tag{3-1}$$

which is quickly followed by:

$$O + O_2 + M \longrightarrow O_3 + M \qquad . \tag{3-2}$$
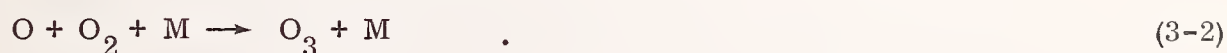
The NO produced in reaction (3.1) is reoxidized by reaction with a hydro-peroxy radical formed during the oxidation of CO or an organic peroxy radical formed by oxidation of a hydrocarbon:

$$CO + OH \longrightarrow CO_2 + H \tag{3-3}$$

$$H + O_2 + M \longrightarrow HO_2 + M \tag{3-4}$$

$$HO_2 + NO \longrightarrow NO_2 + OH \tag{3-5}$$
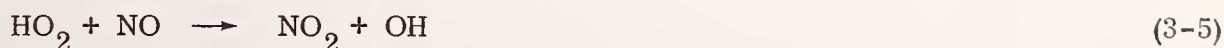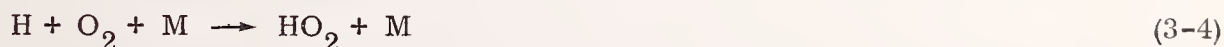
with the net result of reactions (3-1) through (3-5) being:

$$CO + 2O_2 \longrightarrow CO_2 + O_3 \ . \tag{3-6}$$
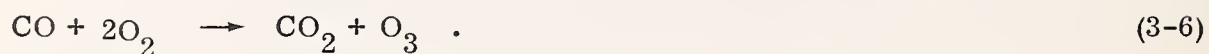
Similar reactions take place involving hydrocarbons. Designating a hydrocarbon molecule as R-H:

$$R\text{-}H + OH \longrightarrow R\cdot + H_2O \tag{3-7}$$

$$R\cdot + O_2 + M \longrightarrow RO_2 + M \tag{3-8}$$

$$RO_2 + NO \longrightarrow NO_2 + RO\cdot \tag{3-9}$$

$$RO\cdot + O_2 \longrightarrow HO_2 + R{=}O \quad , \tag{3-10}$$
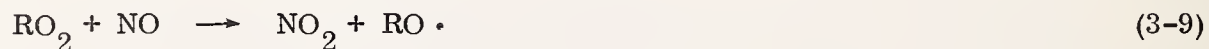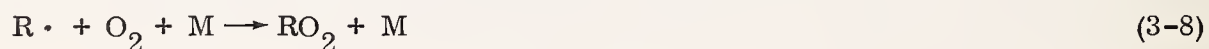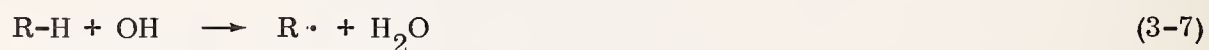
with the NO_2 generated in reaction (3-9) forming ozone via reactions (3-1) and (3-2), and the HO_2 formed in (3-9), reforming OH via reaction (3-5).

Ozone and OH attack on specific hydrocarbon molecules, such as, olefins and aldehydes can lead to the formation of carbonyl radicals, which in turn can form PAN, by reacting with O_2 and NO_2

$$\underset{O}{R\overset{\|}{C}}\cdot + O_2 \longrightarrow \underset{O}{R\overset{\|}{C}OO} \tag{3-11}$$

$$\underset{O}{R\overset{\|}{C}OO} + NO_2 \longrightarrow \underset{O}{R\overset{\|}{C}OONO_2} \qquad (PAN) \qquad . \tag{3-12}$$
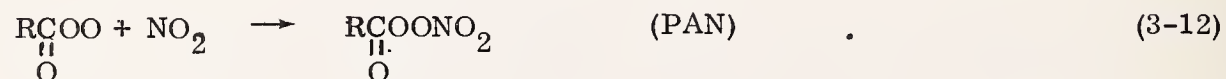
Thus, the very small ambient levels of oxidants, such as, NO, OH and O_3 formed in clean air from the oxidation of naturally occurring fluxes of methane, ammonia, and other biologically produced gases[11,12] can, under solar irradiation, trigger major oxidant pollution levels when supplied with major inputs of NO_x, CO and HC from automotive and other combustion sources.

It should be noted that Equations (3-1) through (3-12) merely sketch the involvement of the regulated automotive emissions in photochemical smog. A fuller account of literally hundreds of reactions needed to fully describe the photochemistry of polluted air can be found in Refs. (7 - 10).

The subtlety of the problem can be appreciated by noting that NO_x emissions in the stratosphere have been predicted to reduce, rather than produce ozone[13,14] The same principle has been noted in very heavily polluted urban atmospheres, where very high initial levels of engine-produced NO can actually destroy local O_3.[15]

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (3\text{-}13)$$

$$NO_2 + h\nu \longrightarrow NO + O \qquad (3\text{-}1)$$

$$O + NO_2 \longrightarrow NO + O_2 \qquad (3\text{-}14)$$

$$O + O_3 \longrightarrow 2O_2 \qquad . \qquad (3\text{-}15)$$
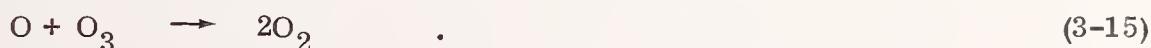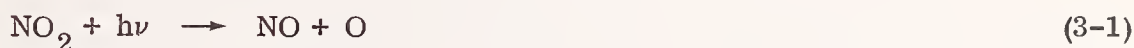
However, reactions (3-13), (3-14) and (3-15), which tend to reduce O_3, do not remain effective in the absence of very high levels of NO_x or O_3, and the O_3 destroyed under very highly polluted conditions is soon regenerated downwind many times over by reactions (3-1) through (3-12) and their companions.

In summary, the currently regulated exhaust emissions are controlled because of their intrinsic toxicity (CO and NO_x) and the major contribution each plays in the formation of photochemical smog under high emission conditions. Further reduction

in each of the regulated automotive emissions, as mandated by the Clean Air Act of 1977, is necessary to restore oxidant and CO levels in urban atmospheres to healthful levels.

A detailed discussion of the chemistry affecting NO_x emissions levels is presented in Subsection 3.3, while NO_x control strategies are presented in Subsection 3.4. More detailed discussions of the chemistry affecting emissions of CO and partially burned or unburned hydrocarbons are presented in Subsection 3.5, with control strategies presented in Subsection 3.6.

3.2 BACKGROUND ON UNREGULATED EMISSIONS

As advances in analytical chemistry allow increasingly detailed and complete characterization of automotive exhaust products, and as our understanding of the long term environmental aspects of atmospheric and biospheric chemistry increases it is very likely that regulation will be imposed on additional automotive exhaust products.

This increased regulation may be a finer tuning of existing rules, for example, restricting only certain classes of unburned hydrocarbons, such as, olefins or aldehydes because of their high reactivity and oxidant-forming potential, or placing special limits on aromatic hydrocarbon emissions because of suspected carcinogenic potential. Or completely new classes of compounds may be brought under regulation because of their potential long term impact on health or climate.

A number of classes of unregulated exhaust compounds have been the focus of discussions in the technical community over the past ten years, because of potential adverse effects on either health or environmental quality. A short review of these discussions is presented in this section. The most serious of these concerns currently involves classes of unburned hydrocarbons produced most copiously in Diesel and other heterogeneous combustion engines. These substances, which include polycylic aromatic hydrocarbons (PAHs) and soot are probably the emissions most likely to be the focus of future EPA regulation. The discussion of unregulated emissions will start with them.

3.2.1 Unburned Hydrocarbons - Special Classes

Incomplete combustion of fuel and lubricating oil exposed to combustion gases can lead to a wide range of compounds composed of hydrogen, carbon, oxygen (from partial combustion) and hetero atoms such as, N or S which depend on fuel or oil composition. These emissions can vary from small fuel fragments, such as, acetylene (C_2H_2) or ethylene (C_2H_4), partially oxygenated fuel fragments, such as, aldehydes (R - $C$$\overset{H}{\underset{O}{}}$), unburned fuel (paraffins, olefins and aromatics), oil fragments, phenols and polycyclic aromatic hydrocarbons (PAHs), malodors, and particulate soot. A number of these compounds have properties which have attracted special attention and which could lead to specific regulation. General chemical considerations and potential reasons for regulation are presented in this section, more detailed chemical considerations affecting emission levels are discussed in Subsection 3.5.

3.2.1.1 Soot

Soot is a graphite-like solid formed by pyrolytic condensation of fuel fragments in fuel-rich zones of combustion systems. Soot generally contains about one percent hydrogen, by weight, giving it an empirical formula of roughly C_8H. It is generally structured into small, roughly spherical particles which vary from 50 to 500 Å in diameter. These individual particles may agglomerate, forming chain-like structures of 0.1 to 10 μm in size. Measurements on Diesel exhausts have indicated that 90% of the the exhausted particulates are less than 1 μm in diameter.[16,17]

In general, heterogeneous combustion systems operate with more extensive fuel-rich regions than homogeneous systems, thus, soot (black smoke) formation is generally far greater in Diesel systems than in current spark ignition engines.

Soot formation is undesirable for a number of reasons: first, as noted above, particles from diesels are predominantly dispersed in submicron sizes against which the human respiratory system has little defense, thus, smaller soot particles may be respirated directly into the lungs, resulting in lung diseases; second, soot particles entrain other high molecular weight unburned hydrocarbon fragments such as PAHs and phenols, possibly protecting these substances from oxidation in exhaust systems and potentially delivering these substances for respiration or ingestion; and third, soot is a dirty substance which degrades visibility and creates grime.

The 1977 amendments to the Clean Air Act require particulate reductions for heavy-duty vehicles by 1981. If Diesel or other homogeneous combustion systems make significant inroads into the light-duty vehicle market it seems reasonable to expect some regulation of soot emissions to be imposed.

3.2.1.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are multiple ring aromatic compounds which can be formed during the pyrolysis of most organic substances. An alternate terminology for these compounds commonly used in the combustion literature is polynuclear aromatic (PNA) compounds.

PAHs are relatively heavy molecules which condense at temperatures characteristic of automotive exhaust systems; thus, PAHs are usually found absorbed on soot particles and otherwise associated with condensed phase exhaust products. The fate of various PAH compounds in exhaust systems has been the subject of a great deal of study. Doping of exhaust flows with ^{14}C labeled PAH compounds has confirmed that PAH chemistry is still very active under exhaust conditions.[18]

The major concern involving PAH emissions is the fact that a number of PAH compounds emitted by automotive and other combustion systems are known to produce cancer in animals and are suspected human carcinogens. The majority of the PAH health effect data are on the compound benzo-α-pyrene (BaP), a chemical commonly detected in both spark ignition and Diesel exhaust.[18,19,20,21]

Quite recently, a great deal of attention has been focused on the potential health effects of PAH emissions from Diesels. This concern was sparked by a study correlating automotive PAH levels with cancer deaths in a Swiss town,[22] and has been sustained by EPA findings of mutagenic activity in the Ames Salmonella Microsome Assay induced by organic solvent extract fractions form Diesel exhaust particulates.[23] It is generally believed that a substance inducing mutagenic activity in the Ames Assay has an 85-90% probability of showing carcinogenic activity in laboratory animals.

While current findings are quite preliminary, it does appear that a serious health threat may arise from PAHs and related heterocyclic and aromatic compounds found in automotive exhausts.[22,23]

3.2.1.3 Benzene, Phenols and Other Light Aromatics

In addition to heavy PAH compounds, the unburned hydrocarbons in exhaust emissions often contain measurable amounts of benzene, phenols and other light aromatic compounds.[19]   In spark ignition engines, this problem has become more acute as the aromatic content of gasoline has been raised to regain antiknock properties lost because of the reduction in tetraethyl lead necessitated by widespread use of catalytic converters.

This concern about light aromatic emissions may be heightened by recent evidence that benzene is a potent leukematic agent. This evidence has triggered a recently imposed emergency reduction in OSHA standards for worker exposure to benzene.

In addition to their health threats, certain substituted aromatics display a very high reactivity in photochemical smog situations. Specific regulation of highly substituted aromatics could be instituted because of their smog initiation potential.

3.2.1.4 Malodors

Anyone ever stalled in traffic behind a Diesel-powered bus or truck realizes that Diesel exhaust emissions can contain objectionable concentrations of foul-smelling substances. Diesel exhaust odor is generally divided into two classes: "oily kerosene" and "smoky-burnt."

Sundry attempts at identifying the chemical constituents responsible for the characteristic Diesel exhaust odors have indicated fuel fragments along with mono and polyoxygenated partial oxidation products,[24]   alkyl napthalenes, alkyl benzenes, indans, tetralins and indenes (oily-kerosene)[24]   and alkyl benzenes and alkyl napthalenes (oily-kerosene) and oxygenated aromatics (smoky-burnt).[26]

Efforts at systematically pinpointing the specific exhaust species responsible for Diesel odors are hampered by the extremely small concentrations of odor causing molecules found in the exhaust gases, the complexity of odor perception, including possible synergistic effects,[25]   the fact that perceived odor level depends heavily on the degree of dilution, and finally the availability of only one instrumental method for quantifying odor levels.

The single instrument for quantifying Diesel odors is based on a liquid chromatography method developed by Levins and co-workers at Arthur D. Little.[26] Correlation of odor intensity predictions from the ADL instrument with judgements of trained odor panels is still imperfect.[27]

The mechanics of instituting regulations on emissions as subjective as malodors is formidable. Since it seems clear that malodors are caused by very low levels of specific unburned or partially oxygenated fuel or oil components, it can be hoped that general measures aimed at reducing other incomplete combustion emissions may reduce malodors to acceptable limits.

3.2.1.5 Aldehydes and Other Oxygenated Hydrocarbons

High levels of aldehydes and other partially oxygenated fuel fragments are thought to be formed in preignition reaction regions in Diesel engines as well as in gasoline engines under autoignition conditions.[29] The degree to which these partially oxygenated compounds survive as exhaust emissions depends on detailed chemistry in the subsequent piston and exhaust train environments.

High concentrations of exhaust aldehydes and other partially oxygenated compounds are generally undesirable from a photochemical smog viewpoint. These compounds have already undergone the first step in the oxidative destruction chain and are considerably more reactive than simple unburned hydrocarbons, such as, paraffins, acetylene, benzene, alkybenzenes or even ethylene.

This high reactivity rating holds if measured on the General Motors NO_2 formation rate scale [30] or the more recently developed OH reaction rate scale.[31]

In addition to their high overall reactivity, aldehydes have a high propensity for the formation of $RCO \cdot$ radicals, which in turn, lead to PAN formation via reactions (3-11) and (3-12).

The high activity of aldehydes in initiating photochemical smog chain reactions could lead to specific regulation of these and similar compounds within the hydrocarbon category.

3.2.1.6 Olefins

Olefins are hydrocarbons containing one or more carbon-carbon double bonds, the simplest and least reactive olefin is ethylene, C_2H_4. Olefins can compose up to 45% of the unburned hydrocarbons from typical spark ignition engines.[30]

The enhanced reactivity of olefins is due to their ability to be oxidized by addition of oxygen containing species across their double bonds. This allows direct olefin oxidation by O and O_3, reactions which are not important for less reactive hydrocarbons.[9]

Because of their enhanced reactivity, any fine tuning of the unburned hydrocarbon regulations could logically place specific limits on olefin emissions.

3.2.2 Nonhydrocarbon Unregulated Emissions

A number of nonhydrocarbon automotive emissions have been postulated to pose specific health or environmental threats.

Control of a number of these emissions can be achieved by careful selection or control of fuel or oil additives or impurities, and thus, lie outside the main scope of this review. They have been included in this section for completeness.

3.2.2.1 Carbon Dioxide (CO_2)

A great deal of recent attention has been focused on the well documented rise in atmospheric CO_2.[32-34] The current atmospheric burden of CO_2 is approximately 330 ppm and is growing at a rate close to one percent per year.

A possible threat to current automotive technology is the increasing awareness that carbon dioxide (CO_2) may not be as environmentally benign a substance as has been commonly assumed. If the current concerns over the climatic implications of increasing atmospheric levels of CO_2 prove real, the implications for all combustion systems, not just internal combustion engines is quite serious. The removal and storage of a major exhaust species, such as, CO_2 would pose a significant obstacle to any combustion driven transport system.

The major source of the present rise in atmospheric CO_2 is the addition of fossil fuel exhaust products to the atmosphere, although some authors feel that slash and burn methods of jungle land clearing also add significant amounts.[33] Almost any gaseous carbon containing molecule will undergo photochemical oxidation to CO_2 in the earth's atmosphere through reactions like (3-3), so from the standpoint of global CO_2 levels, it matters very little whether the carbon in exhaust emissions is in the form of CO_2, CO or unburned hydrocarbons. The actual atmospheric levels of CO_2 are set by complex and incompletely understood interactions between the atmosphere, the biosphere and the oceans.[32 - 34]

The chief environmental effect of additional atmospheric CO_2 is the additional trapping of infrared radiation from the earth's surface as it tries to reradiate the visible light received from the sun. This so-called ''greenhouse effect'' is thought to be capable of significantly increasing the earth's average temperature, particularly in the polar regions, if atmospheric CO_2 levels continue to climb at present rates. The climatic effects of this warming are largely unknown, but significant decreases in the mass of polar ice caps causing significant rises in the sea level are thought likely.[35]

The current level of knowledge about global climate problems, such as, the CO_2 greenhouse effect is not sufficient to predict either the extent of the CO_2 problem, or the impact it might have on transportation technology. It is safe to predict that internal combustion-powered light-duty vehicles will be with us for some time to come, and research should continue on optimizing this form of transportation. It should be noted that the potential CO_2 problem gives increased importance to the already crucial question of fuel economy. More miles per gallon translates nicely into less exhaust CO_2 or CO_2 precursors per mile.

3.2.2.2 Nitrous Oxide

Unlike the other oxides of nitrogen, nitrous oxide, or ''laughing gas'' is quite non-toxic and does not participate to any significant extent in photochemical smog formation. However, N_2O is involved in two major global environmental concerns. First, N_2O released at ground level finds its way to the stratosphere where it reacts

to form nitric oxide.[36,37] This nitric oxide, NO, in turn catalytically destroys stratospheric ozone through reactions (3-13, 3-14, and 3-15). Secondly, tropospheric N_2O acts much like CO_2 and future man-induced increases in atmospheric N_2O may lead to a second "greenhouse effect" type problem.[38]

Nitrous oxide is emitted from combustion sources,[39,40] and is particularly effectively produced by certain automobiles equipped with catalytic converters.[40,41] Current levels of automotive N_2O production are not important when compared to other anthropogenic sources;[36,41] nevertheless, care should be taken that engine combustion and exhaust systems do not significantly exceed current N_2O production levels.

3.2.2.3 Cyanide Compounds

Because of their extreme toxicity, compounds containing the cyanogen (CN) functional group may cause special concern when exhausted into the environment. It is known that pyrolysis of simple hydrocarbons[43] and aldehydes[44] in the presence of nitric oxide can form hydrogen cyanide (HCN) and acetonitrile (CH_3CN).

It is also now known that simple flame radicals such as CH and CH_2 are probably capable of fixing N_2 and forming CN:

$$CH + N_2 \longrightarrow HCN + N \qquad\qquad (3-16)$$

$$CH_2 + N_2 \longrightarrow HCN + NH \qquad . \qquad\qquad (3-17)$$

Reactions like (3-16) and (3-17) have been identified as precursors to ''prompt'' NO formation.[45,46]

It appears that the efficiency of cyanide compound production (and destruction) varies widely from engine to engine. Schuchmann and Laidler[47] found less than 1 ppm of HCN and CH_3CN in the exhaust of a 1963 Ford Anglia engine, while Myerson and Blair found 7-8 ppm in the exhaust of a 1970 Ford 302 V8 engine.[48] It has been noted that that exhaust of cars equipped with certain types of catalytic converters can

contain several hundred ppm of HCN[49] High levels of HCN production were also obtained by Myerson and Blair when they injected excess ethane into their automotive exhaust[48]

The real worry may be that heterogeneous combustion engines with local fuel-rich regions may produce significant amounts of HCN through reactions like (3-16) or (3-17). If this cyanide is not consumed in subsequent combustion or exhaust reactions, it could cause potential regulatory problems. The fate of HCN emitted to the atmosphere is unclear, since the usual breakup pathway for hydrocarbon species (reaction with OH) is not available for HCN. Presumably rainout and decomposition by soil bacteria is the ultimate fate of exhausted hydrogen cyanide.

3.2.2.4 Sulfates and Sulfur Dioxide

Sulfur is a minor impurity in Diesel fuel and gasoline, typically comprising 0.03 wt. % in gasoline[50] with a government limit of 0.1%,[29] and regulated to between 0.05 and 0.20% for 1-D Diesel fuel and between 0.2 and 0.5% for 2-D Diesel fuel[29] Since the sulfur levels in both gasoline and Diesel fuels are far lower than those found in stationary combustor fossil fuels such as coal and fuel oil, the SO_2 levels produced by automotive sources are a small portion (<1%) of those produced by stationary combustors, and are consequently not regulated. However, if light-duty Diesel engines assume a major portion of the US automotive market, federal regulations on Diesel fuel sulfur content may have to be lowered to that currently in effect for gasoline.

Ordinary gasoline and Diesel engines emit most of their exhaust sulfur as SO_2, a relatively harmless gas until it undergoes further oxidation. Gasoline engines equipped with catalytic oxidation converters designed to reduce CO and HC levels also oxidize an appreciable amount of their exhaust sulfur to sulfuric acid and sulfate particulates[29,50]

The platinum catalysts currently used in converters efficiently oxidize SO_2 to SO_3:

$$SO_2 + 1/2\ O_2 \longrightarrow SO_3 \tag{3-18}$$

and SO_3, the anhydride of sulfuric acid, quickly combines with water vapor to form sulfuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad \cdot \tag{3-19}$$

Finally, below exhaust temperatures of $540^{\circ}C$, condensation of aqueous sulfuric acid takes place, typically forming aerosol droplets less than $0.25\ \mu$ m in diameter.[50]

These respirable sulfate particles are a direct threat to health and their buildup along highways must be avoided. Actual prediction of the level of sulfate particulate buildup in the atmosphere along highways involves complicated questions of vehicle mix, traffic patterns, aerosol growth and agglomeration, and dispersion. This question has been attacked by an EPA/General Motors experiment involving extensive measurements and modeling efforts.[51,52,53]

3.2.2.5 Lead Particulates

Leaded gasolines contain up to 3 g/gal of tetraethyl or tetramethyl lead as an anti-knock additive. Combustion of this fuel typically results in 0.1 to 0.5 grams of lead per mile with an appreciable portion of the lead remaining deposited in the cars engine oil and exhaust system.[50] The lead emitted is mostly in the form of lead bromide or lead chloride particles, sometimes associated with ammonium halides. About 80% of the lead particles are less than $2\ \mu$ m in diameter and 40% are below $0.2\ \mu$ m.[50] The halogen content of the particles arises from ethylene dichloride or ethylene dibromide added to gasoline as lead scavengers. The toxic effects of ingested lead are well known; however, the health hazard of automotive exhaust lead are currently under intensive debate. The degree of movement of exhaust lead into the food chain is currently unknown.

It is true that the increased use of low lead gasoline necessitated by the require-
ments of catalytic exhaust converters has reduced automotive emissions of lead to
the environment. Pending federal regulations would reduce lead to 0.8 g/gal in 1978
and 0.5 g/gal by October 9, 1979, with certain exceptions for small refiners. Of
course, significant shifts to Diesel engines would also tend to eliminate the lead
emission problem.

3.3 NO_x PRODUCTION CHEMISTRY

A general agreement on the chemical kinetic mechanisms governing NO_x
production in internal combustion engines, as well as other combustion sources has
been reached during the last several years. Thus, the same NO_x reaction sequences
and kinetic data are discussed in recent reviews on pollutant formation in general
combustion processes[54] pollutant production in spark ignition engines[50] and
pollutant formation in Diesel engines.[29,55]

3.3.1   Modified Zeldovich Mechanism

Under conditions of normal fuel-to-air ratios, and in the absence of major
amounts of chemically-bound nitrogen in either the fuel or fuel additives, it now
seems clear that the bulk of the NO_x production arises from the "modified Zeldovich"
mechanism. The original Zeldovich mechanism[56] explains the fixation of molecular
nitrogen by atomic oxygen at high temperatures:

$$O + N_2 \longrightarrow NO + N \quad , \tag{3-20}$$

$$N + O_2 \longrightarrow NO + O \quad . \tag{3-21}$$

Lavoie and co-workers[57] have extended the basic Zeldovich mechanism to include
the reaction:

$$N + OH \longrightarrow NO + H \tag{3-22}$$

-26-

which can contribute under stoichiometric and fuel-rich conditions. Evaluated rate constants from Ref. (49) for these reactions are shown in Table 3-2. The key reaction in the mechanism is (3-20), which has a combined endothermicity and activation energy of 76 kcal/mole[50]. Thus, to be effective, the modified Zeldovich mechanism relies on both atomic oxygen and very high temperatures, since the rate of reaction (3-20) varies as $\exp - (38,000/T(^{o}K))$.

Reactions (3-20) through (3-22) ensure the production of appreciable amounts of NO in air fed combustion systems operating under lean, stoichiometric and even somewhat fuel-rich conditions. At high temperatures, reactions (3-21) and (3-22) are both very rapid, thus reaction (3-20) is the rate-controlling reaction under most combustion conditions.

Unfortunately, the reverse processes for reactions (3-21) and (3-22) are also quite endothermic; and back conversion of NO to N_2, O_2 and OH can easily become kinetically frozen in fast-cooling exhaust gases. This often leads to supraequilibrium concentrations of NO in combustion exhaust flows.

A number of calculational models have been developed to model NO formation under the conditions appropriate to internal combustion engines. These models have been recently reviewed by Heywood,[50] Henein,[29] and Raine et al.[55] Most models employ steady state assumptions, and assume that O, OH, and H are in local partial equilibrium. As a result of these assumptions, local rates of formation for NO can be represented by an analytical expression involving the rates of reactions (3-20), (3-21) and (3-22) and the equilibrium constant, $K_{(3-23)}$, for the conversion of N_2 and O_2 to NO:

$$ N_2 + O_2 \longrightarrow 2\,NO \qquad . \tag{3-23} $$

Thus:

$$ \frac{d\,[NO]}{dt} = 2k_{(3-20)}\;[O][N_2]\;\frac{1-[NO]^2/K_{(3-23)}\;[O_2][N_2]}{1 + k_{(3-20)}\,[NO]/k_{(3-21)}\,[O_2]k_{(3-22)}\,[OH]}^{(55)} \tag{3-24} $$

-27-

TABLE 3-2   EVALUATED RATE CONSTANTS FOR MODIFIED ZELDOVICH REACTIONS[54]

	Reaction	Rate Constant (cm^3/sec)	Valid Temperature Range
(3-20)	$O + N_2 \longrightarrow NO + N$	$1.3 \times 10^{-10} \exp(-38,000/T)$	2000 – 5000
(3-20)	$N + NO \longrightarrow N_2 + O$	2.7×10^{-11}	300 – 5000
(3-21)	$N + O_2 \longrightarrow NO + O$	$1.1 \times 10^{-14} \, T \exp(-3150/T)$	300 – 3000
(3-21)	$NO + O \longrightarrow O_2 + N$	$2.5 \times 10^{-15} \exp(-19,500/T)$	1000 – 3000
(3-22)	$N + OH \longrightarrow NO + H$	1.7×10^{-10}	300 – 2500
(3-22)	$H + NO \longrightarrow OH + N$	$3.3 \times 10^{-10} \exp(-23,650/T)$	2200 – 4500

While Equation (3-24) is often adequate to predict the NO production under many conditions, it must be used with some caution. For instance, it is often assumed that concentration values for the flame radicals O, OH, and H are equilibrated with molecular concentrations at the local flame temperature. However, under both lean and rich flame conditions, radicals such as O and OH can overshoot their equilibrium values,[39,60,61] thus resulting in NO production different from that calculated under equilibrium assumptions.

While it is often true that due to slow recombination rate constants flame radicals are not in equilibrium with their molecular precursors, it is frequently true that they are in partial equilibrium with each other. This fact can often be used in conjunction with Equation (3-24) to arrive at satisfactory NO production calculations.[55]

3.3.2 "Prompt" NO

As noted in Subsection 3.2.2.3, in certain flame systems, N_2 may be fixed by reaction with hydrocarbon flame radicals. These "prompt" NO initiation reactions (3-16 and 3-17) lead to the production of HCN, N, and NH, all of which may be oxidized in subsequent reactions to form NO.[45,46]

While this "prompt" NO is not a major contributor to the total NO produced in normal stoichiometric or lean engine operation, it may be an important factor in staged or stratified combustors. Systems employing fuel-rich initial combustion zones in order to hold down Zeldovich mechanism NO by suppressing temperature and O atom levels, may have to contend with enhanced "prompt" NO production.

3.3.3 Fuel N Derived NO

The final NO_x production mechanism of potential interest to internal combustion engine systems is the oxidation of bound nitrogen in fuel, fuel additives or engine oil. The production of NO from fuel-bound heterocyclic or amine nitrogen atoms can be a very efficient process, particularly under lean combustion conditions.[62,63] The low level of fixed N in petroleum-derived gasoline and Diesel fuel prevents this mechanism from contributing significantly to total NO production. The level of fixed N in future synthetic fuels derived from high nitrogen sources such as coal and

shale oil may have to be regulated to prevent significant fuel nitrogen-derived NO from being formed. Furthermore, nitrogen containing Diesel fuel additives must be evaluated for fuel NO production significance.

3.4 NO_x EMISSION CONTROL STRATEGIES

Since the major source of IC engine-produced NO are attributable to the modified Zeldovich mechanism,[29,50,55] NO_x control strategies must either contradict this formation mechanism or rely on exhaust gas cleanup. The exhaust gas clean-up strategies, which are currently limited to either catalytic NO_x reduction units[50] or conceivably homogeneous gas phase exhaust reactions involving either hydrocarbon[48] or ammonia[64] injection, are beyond the scope of this report. The discussion below will concentrate on techniques which suppress Zeldovich mechanism NO production.

3.4.1 Adjustment of Fuel/Air Equivalence Ratio

Because of the critical dependence of reaction (3-20) on temperature, high NO production is closely tied to high combustion chamber temperatures. Thus, NO production in conventional spark ignition and Diesel engines is closely tied to the local fuel-air equivalence ratio, which has a strong and direct impact on combustion temperature.

In a conventional spark ignition engine, NO production generally peaks at air-fuel ratios near 16, just to the lean side of stoichiometric.[50] Unfortunately, slightly lean equivalence ratios are very desirable from the viewpoint of minimizing HC and CO production. If emissions from incomplete combustion and fuel economy were not considerations, major reductions in exhaust NO emissions could be achieved by simply adjusting the fuel/air equivalence ratio to either a lean or rich condition.

With regard to heterogeneous combustion systems, it must be remembered that it is the O/F ratio of each combustion gas element that counts, an overall lean mixture can still produce high NO levels if hot, near stoichiometric regions exist within the mixture, and are not quickly cooled by turbulent mixing after combustion.

-30-

3.4.2 Exhaust Gas Recirculation and Compression Ratio

The major NO reduction mechanisms employed in currently-produced spark ignition engines are exhaust gas recirculation (EGR) and reduced compression ratio. Diluting the combustion charge with recirculated exhaust gas is a direct method of lowering combustion gas temperatures by diluting the air/fuel mixture with inert, poly-atomic gas, thus lowering energy, density, and flame speed.[50] The resulting reduction in temperature restricts reaction (3-20), shutting off higher levels of NO production.

3.4.3 Adjustment of Other Engine Parameters

Since temperature plays such a key role in NO production, adjustment to any operating parameters which lower peak combustion temperatures will tend to lower NO emissions. Combustion temperatures can be lowered by slowing flame speeds, increasing mixing, or increasing heat transfer to chamber walls. According to Heywood,[50] other important engine design and operating variables which affect NO emissions from spark ignition engines include engine speed, inlet mixture pressure and temperature, spark timing and combustion chamber geometry through effects on flame speed and length of flame travel

Because many of these parameters also severely affect fuel economy, engine knock characteristics, and emissions of CO and HC due to incomplete combustion, engine optimization is obviously a difficult procedure.

3.4.4 Staged Combustion

Indirect injection Diesel engines, in general, produce less NO than direct injection units. This reduction in NO is generally attributed to the ability of the indirect injection engine to run more retarded.[29]

In general, staged combustion schemes with prechamber burning allow a second degree of freedom in adjusting combustion temperatures and equivalence ratios. This type of strategy is widely used in aircraft turbine engines and is discussed further in Section 5.

3.5 CHEMISTRY OF EMISSIONS DUE TO INCOMPLETE COMBUSTION

3.5.1 Homogeneous Versus Heterogeneous Combustion Systems

Carbon monoxide and all of the classes of incompletely burned hydrocarbon emissions detailed in Section 3.2 could be controlled if complete combustion were achieved under lean or stoichiometric conditions.

In principle, many types of incompletely burned hydrocarbon emissions may be relatively easy to control in homogeneous combustion systems. In a homogeneous system very few fluid elements have either unusually high or unusually low fuel content. Thus, if NO production were not a problem, emissions of CO and unburned hydrocarbons could largely be eliminated by operating under lean conditions, with wall quench regions remaining the major source of incompletely oxidized hydrocarbon emissions. As will be shown below, the situation for heterogeneous combustion systems is considerably more complex.

3.5.2 CO Oxidation Chemistry

The principal reaction responsible for the oxidation of CO in engine combustion and exhaust systems is the same reaction identified in Section 3.1 as the atmospheric sink for CO:

$$CO + OH \longrightarrow CO_2 + H \tag{3-3}$$

While CO is probably in equilibrium with other combustion gases at peak cycle temperatures, in stoichiometric and lean systems, reaction (3-3) does not seem to be able to keep CO levels in equilibrium as the gas cools during the expansion stroke and exhaust process.[50] The reasons for these supraequilibrium levels of CO are not completely understood, and may include wall quench and boundary layer entrainment as discussed below.

-32-

3.5.3 Wall and Boundary Layer Quench Effects

The surfaces of the interior cylinder walls and the piston head are all much cooler than the combustion cylinder gases during most of the piston cycle. It is widely believed that under normal spark ignition operating conditions, the quench layers along, and the crevices between these cool surfaces are responsible for the partially burned and unburned hydrocarbon emissions.[50] Surface effects are further complicated by the presence of thin films of lubricating oil which may be degraded and entrained into boundary layer flows, adding to the hydrocarbon emissions.

Quench layers on the order of a few thousandths of an inch thick have been measured in photographic studies of cylinder combustion. Presumably, rapid destruction of flame-oxidizing radical in the cool environment freezes out the burning process in these layers. This freezing process leaves behind a varied mixture of unburned and partially burned fuel and oil species, as well as fuel and oil pyrolysis products. Over 200 organic compounds have been identified by gas chromatographic analysis of spark ignition engine exhaust.[50]

These same wall quench effects also play a role in hydrocarbon emissions from Diesel engines,[29] with the added complication that in many engines unvaporized fuel droplets impinge directly on cylinder surfaces, adding to the hydrocarbon burden of the quench layers.

Unfortunately, as discussed below, heterogeneous combustion systems have additional sources of hydrocarbon emissions.[29]

3.5.4 Diesel Combustion Model

Henein has recently outlined a phenomenological model of combustion in direct injection Diesel engines that nicely illustrates the additional combustion regions which may produce significant quantities of CO and/or hydrocarbon emissions in these systems.[29] Henein's model of direct fuel spray injection into a combustion chamber has five generic regions, each with its suspected emissions problems; they are each described below.

-33-

3.5.4.1 Lean Flame Region

Smaller drops in the fuel spray tend to preferentially reach the outer and downstream edges of the fuel jet, where they vaporize and mix with the air charge. This outer region of the fuel spray is the first area to reach self-ignition limits, and photographic evidence shows that Diesel combustion starts within this spray envelope.[29]

The average mixture in this lean flame region is oxygen-rich, and it is not a significant source of CO or hydrocarbon emissions; however, it is thought to be a region where high concentrations of NO are produced.

3.5.4.2 Lean Flame-out Region

Just beyond the lean flame region is a largely homogeneous region where the equivalence ratio is so lean that combustion cannot be supported. Fuel penetrating this region is either unreacted or undergoes preignition oxidation reactions to form aldehydes and other partially oxygenated hydrocarbons. Carbon monoxide diffusing into this region is not oxidized to CO_2. Henein suggests that this region resembles the quench zones responsible for hydrocarbon emissions in spark ignition engines.[29]

3.5.4.3 Spray Core

The central region of the fuel jet contains the larger fuel droplets and the highest density of fuel. The combustion in this region is initiated by heat radiated and convected from surrounding lean flame region and its evolution critically depends on the turbulent mixing of the core with the surrounding air. Local fuel-rich regions, possibly including areas containing incompletely vaporized fuel droplets, represent rich potential sources of emissions including CO, aldehydes, malodors, unburned fuel, PAHs and soot.

Unfortunately, the details of the pyrolysis and partial oxidation reaction mechanisms leading to the various classes of hydrocarbon emissions are not well understood.[29,54,55] It is thought that pyrolysis reactions in fuel-rich regions lead to high concentrations of hydrocarbon radicals. If insufficient oxygen reaches these regions, the hydrocarbon radicals can condense to form aromatic hydrocarbon

-34-

molecules significantly larger than those found originally in the fuel, including PAHs. Extremely fuel-rich and hot regions are sources of soot, which can be viewed as very large pyrolysis-induced condensation products.[45]

Again, it should be emphasized that the understanding of the reaction mechanisms leading to malodor, PAH, and soot formation are much less developed than the mechanisms governing NO_x or CO production. Consequently, attempts to model formation of heavy hydrocarbon emissions have been largely unsuccessful.[50]

The degree to which CO and hydrocarbon species formed in the spray core contribute to final exhaust emissions levels depends on detailed mixing and chemical processes which occur during the expansion and exhaust processes. Unfortunately, very little is known about the details of the oxidation chemistry which occurs under these conditions.[18] The production of PAHs does seem to be positively correlated with the aromatic content of the fuel.[19]

3.5.4.4 Spray Tails and Secondary Injections

The last fuel injected in current Diesel units is often in the form of large droplets, due to the small pressure differential acting at the tail end of the injection process.[29] Under high load conditions, these spray droplets are not mixed with sufficient oxygen to ensure effective combustion. Thus the spray tail represents a particularly fertile region for formation of CO and the various classes of incompletely oxidized or unburned hydrocarbons.

If injection valves are not designed properly, they may allow fuel to continue to dribble into the combustion chamber late into the expansion stroke. The results are identical to the spray tail situation, with unburned fuel and pyrolysis products being injected into the exhaust flow.[29]

3.5.4.5 Wall Effects

Wall effects in heterogeneous combustors are similar to those described for spark ignition quench layers in Subsection 3.5.3. One additional complication is that unvaporized fuel droplets may reach the wall and contribute to its hydrocarbon loading.

The entrainment of wall boundary layer gases is complex and is obviously affected by the details of combustion chamber geometry and its effects on fluid mixing processes.

3.5.5 Role of Fluid Mixing Processes in Hydrocarbon Emissions

The production of CO, unburned hydrocarbons, partially oxidized hydrocarbons, and hydrocarbon pyrolysis emissions all depend on the existence of regions which are either locally rich, lean, or cold.

The existence of such regions is due to detailed fluid mixing processes and the control of such regions is also largely a matter of detailed fluid mechanics. This point will be expanded upon in Sections 4 and 5.

3.6 INCOMPLETE COMBUSTION CONTROL STRATEGIES

The master control strategy for emissions of CO and the various hydrocarbon classes is obvious: simply ensure complete combustion.

As indicated in the previous section, complete combustion depends largely on the effective transport of heat, fuel and oxygen within the combustion chamber. As indicated in Section 6, these mixing processes can be optimized, even for heterogeneous combustion systems, with dramatic results. However, this is a complex task, requiring extensive experimental and theoretical efforts.

Since the detailed kinetic mechanisms controlling certain classes of incomplete combustion emissions are unknown, the degree of mixing needed to eliminate malodors, PAHs, and soot, for instance, are not known.

Research opportunities which could yield needed data on pertinent fluid dynamic and chemical kinetic processes are detailed in Section 6.

3.7 ROLE OF LUBRICATING OIL IN EMISSIONS PROBLEMS

The role of lubricating oil in higher weight hydrocarbon emissions such as maladors, PAH's and soot is unclear. At least one study has found a positive correlation between lubricating oil consumption and PAH emissions.[65]

Detailed studies aimed at elucidating the role of lubricating oil in the production of unregulated hydrocarbon emissions are outlined in Section 6.

3.8 ROLE OF NONHYDROCARBON IMPURITIES AND ADDITIVES IN EMISSION CHEMISTRY

As outlined in Subsection 3.2.2, the production of certain emitted pollutants, such as, lead particulates, SO_2 and sulfate particulates, are a direct result of additives or impurities in fuel. Current federal regulations on sulfur in gasoline (0.03 wt. %) insure that SO_2 and sulfate emissions from automobile exhaust comprise only about 1% of the total sulfur emitted by combustion sources. Thus, there is very little environmental gain to be realized by lowering gasoline or Diesel fuel sulfur below this standard. This category of pollutants can also be extended to NO_x produced from bound nitrogen in fuel or fuel additives.

For mobile sources, the efficient control of these types of pollutants is most easily assured by regulation of fuel composition, rather than by adjustment of combustion parameters or the addition of exhaust reactors.

3.9 EMISSIONS MEASUREMENTS TECHNIQUES

The efficiency of research on any pollutant is often strongly tied to the ease and accuracy of measuring that pollutant in combustion and exhaust systems.

3.9.1 Measurement of Light-Weight Gaseous Pollutants

Extremely accurate and relatively uncomplicated analytical techniques exist for quantifying the levels of NO, NO_2, CO, SO_2 and several light unburned hydrocarbons for both grab samples and in situ measurements. Established techniques include gas chromatography, quantitative infrared spectroscopy, mass spectroscopy, and in certain cases, visible and UV resonance fluorescence and chemiluminescent analysis. Current methods of choice include: ozone chemiluminescent techniques for NO_x, quantitive infrared spectroscopy for CO, UV resonance fluorescence for SO_2, and flame ionization gas chromatography or infrared spectroscopy for light hydrocarbons, such as, methane, ethane, ethylene, actylene, aldehydes, propane, propene, butanes, butenes, and benzene.

Exhaust dilution techniques which are well suited for sampling stable, gaseous species are also well established. Since air pollution monitors for very low levels of most small, stable pollutants have been developed, the relatively high levels of CO, NO_x, SO_2, and light hydrocarbons found in even diluted exhausts can be measured with relative ease.

3.9.2 Measurement of High Molecular Weight and Particulate Pollutants

Unfortunately, the measurement of high molecular weight species is not so straightforward. This is true for a number of reasons: the actual amounts of heavy pollutants such as malodors or PAHs are usually very low; the small amounts of heavy pollutant materials within a given class are usually divided into a number of different molecular species, each having slightly different chemical and physical properties and conceivably very different environmental or health effects; high molecular weight compounds are often associated with and must be separated from particulate emissions such as soot; and finally, complex organic compounds may continue to undergo chemical reaction through the exhaust process, making the measurement result highly dependent on the point and mehtod of sampling.

PAH detection and quantification is an illustrative case. Recent attempts to measure PAH concentrations in Diesel exhausts and correlate PAH emissions with operating conditions have been fraught with uncertainty.[24] However, careful application of such classical analytical techniques, such as, gel filtration, gas and liquid chromatography, mass spectroscopy and ultraviolet spectroscopy have been successfully employed to separate, identify and quantify components of complex environmental PAH mixtures.[22,66,67] It should be recognized that these complex analytical techniques are time-consuming and subject to error. A similar situation exists with regard to the identification and quantification of exhaust malodors,[23,24,25] where there is a continuing effort to develop reliable instrumentation.

The sampling and characterization procedures for particulate materials are also often complex and tedious. Major advances have been made in instruments for systematically determining particulate size distributions.[17] However, detailed particle chemical characteristics can require major effort.

-38-

In summary, sampling techniques and analytical instrumentation do exist which allow quantitative exhaust emission studies for difficult species, such as, PAHs, malodors, and soot. However, in situ measurement techniques have not, in general, been demonstrated. Measured emission levels for these species are extremely sensitive to sampling techniques, and careful attention must be paid to the design of suitable sampling methods.

It should be recognized that significant efforts will have to be devoted to the development and calibration of suitable analytical techniques if studies on the formation and suppression of these types of unregulated emissions are to be successful.

4. COMPETITION OF HOMOGENEOUS VERSUS STRATIFIED CHARGE ENGINES

The relative advantages and disadvantages of homogeneous and stratified combustion engines are implicit in the above discussion. The purpose of this section is to state them somewhat more explicitly.

From the standpoint of emissions, the homogeneous system has the advantage that there are no fluid elements of unusually high or low fuel content, which can lead to high temperatures and excessive NO_X production, or to CO and unburned hydrocarbons. Thus, it offers a high degree of predictability in the combustion process. The lean ignition limit for the homogeneous mixture prevents operation at as lean mixtures as would be desirable to fully control NO_X emissions and this makes exhaust gas recirculation necessary to control the NO_X. Furthermore, quench layers on the combustion volume walls limit the actual homogeneity.

Stratified combustion makes operation at very lean overall mixtures possible. It does so by introducing variations in composition which lead to stable combustion but also to locally high rates of pollutant production. Control of emissions then depends on the details of injection and mixing which control the local composition and temperature histories of fluid elements.

From the standpoint of fuel economy, the principal disadvantage of the homogeneous engine is that the lean combustion limit leads to unnecessarily high combustion temperatures at light load conditions. These high temperatures degrade the efficiency through the increased specific heat of the combustion gases. A second effect of the lean limit is the requirement for throttling, which lowers the efficiency by introducing pumping losses.

It seems likely that if the lean limit could be extended to allow unthrottled operation of the homogeneous engine at low load conditions, its advantages of charge uniformity and simplicity (assuming that this is maintained) would make it preferable to the Diesel or stratified charge engines. This will require innovation based on

increased understanding of the chemical kinetics and fluid mechanics of the homo-
geneous combustion process. The Diesel and stratified charge engines, on the
other hand, should benefit from a systematic research and development program
which proceeds by building an understanding of the thermal, fluid mechanical and
chemical processes which control the heterogenous combustion process. The
program, outlined below, deals appropriately with each type of combustion system.

5. TECHNOLOGY TRANSFER FROM GAS TURBINE COMBUSTORS TO HETEROGENEOUS COMBUSTION PISTON ENGINES

The combustion of liquid petroleum fuel in gas turbines is usually accomplished by injection of a spray of liquid droplets into the air stream where the droplets vaporize, the fuel vapor mixes with the air by laminar and turbulent diffusion and chemical reaction occurs in regions of nearly stoichiometric composition. Since the overall air fuel ratio is much higher than stoichiometric, the combustion products are then cooled by dilution with excess air. Each of the processes described must occur in some way in Diesel engines, where the fuel is injected into the cylinder as a spray of liquid droplets, and in stratified charge engines which use cylinder-injection of fuel, such as the Texaco Controlled Combustion Process[5] and the Ford-Proco system.[29] Some of the processes are bypassed by stratification schemes where two different gas mixtures are formed by carburation,[4] but the near-stoichiometric combustion followed by mixing and cooling remains.

In the development of gas turbine combustors, a great deal of effort goes into the evolution mainly by trial and error of air flow patterns which will provide the residence time and turbulence levels required to insure stable, complete combustion with pollutant emission levels which are acceptable. These air flow patterns are obtained by shaping the combustor liner so as to produce strong vortices, recirculation zones and dilution jets. To obtain satisfactory performance at one engine operating condition such as full power is difficult and striking compromises required for successful operation at all conditions from idle to full power is difficult in the extreme. As the air inlet temperature, pressure, and flow velocity change with power level the combustion system must maintain the residence times and mixture compositions required for complete combustion with acceptable pollution.

All aircraft gas turbines now operational have met these requirements with combustors of fixed geometry, except that in some, two-stage fuel nozzles have been used to produce good atomization over a wide range of fuel flows. But, it will not be possible to meet the 1979 EPA airport emissions requirements with such combustors.[69,70]

The NASA Clean Combustor Program has led to the definition of advanced combustors in which one flow path is used for idle and low speed operation while a second flow path is activated for full power.[71, 72] This makes it possible to have low enough flow velocities for good combustion efficiency at low power and still high enough velocities (low residence times) at full power to limit the NO_x production. It is generally assumed that a broader range of variability will be required to satisfy the very low NO_x requirements which may be set for supersonic stratospheric cruise aircraft.

A better idea of the relative degrees of difficulty of the emission control problems for aircraft and for automobiles can be gained by comparison of the goals in the two systems. For autos the goal is 0.4 grams NO_x per mile. For aircraft the goal of the NASA SCERP (Stratospheric Cruise Emissions Reduction Program) is 1 to 2.5 gram per kilogram of fuel.[70] The conversion is:

$$\frac{g\ (NO_x)}{kg\ (fuel)} = \left(\frac{grams}{mile}\right)\left(\frac{miles}{gal}\right)\left(\frac{gal}{kg}\right) \approx (0.4)\ (20)\ (\frac{1}{3}) = 2.6$$

So the objectives are of comparable difficulty.

The main point to be drawn from this analogy is that control of the emissions and combustion efficiency in a heterogeneous combustion process requires control, if not complete understanding, of the fluid mechanical processes throughout the combustion process. Whereas, the flow changes from idle to full power in a gas turbine, it changes continuously throughout the cycle in a piston engine, and these cyclic changes are in addition modified by load and speed variations. To achieve a degree of control in piston engines comparable to that in aircraft gas turbines it will be necessary to develop a detailed understanding of the fluid mechanics of the engine processes and of the interaction between the injected fuel and the air flow.

When such an understanding becomes available, the large gas turbine combustor technology base should be transferable to a considerable degree to piston engines. More explicity, if it is possible to describe the variation with time of the pressure, temperature, and turbulence level of each fluid element after fuel is injected into it, it should be

possible to predict the final composition of each element and of the final mixture. A
rational development program could then be build around theoretical and experimental
study of the critical portions of the processes.

6. RESEARCH OPPORTUNITIES

As outlined the the previous sections, there are many opportunities for reducing automotive fuel consumption and emissions. Since there is, in many situations, a tension between these two and since increases in cost are usually associated with the required modifications, quantitative understanding is required for making the systems design choices in a rational way. The research opportunities lie in establishing this quantitative understanding.

A comprehensive program must have as its objective quantification of all important aspects of the system to approximately the same level of precision. Thus, we must consider:

1. The characteristics of the engine,

2. The drive train and its impact on engine requirements, fuel consumption and emissions,

3. The effect of actual usage on the system fuel consumption and emissions.

Present understanding of all three aspects is only qualitative. Considering first the engine, a thorough and very systematic review of stratified charge engines has been carried out by Ricardo[3] for EPA. The report describes in quantitative terms the performance and emissions of a large number of engine configurations. It also contains qualitative explanations for the differences between the various engines. It does not provide a quantitative connection between the engine configurations and their performance and emissions. The development of this quantitative connection is a prerequisite to rational design optimization, and the principle objective of the research program outlined below.

The effect of the transmission on actual system fuel consumption is also only understood qualitatively. For example, it is commonly supposed that manual transmissions will deliver better fuel economy than automatics because of the lower efficiency of the latter. But, in actual usage this is not clear because the automatic may do a much better job of controlling shift points, thus minimizing excess engine friction and throttle movement.

Obviously, aspects (2) and (3) are coupled as indicated previously, but (3) contains other factors, such as, maintenance practices, warmup procedures, excessive idling, etc.

This report will subsequently deal only with research opportunities in the engine, not because it is the only critical element, but because others presumably are dealing with transmissions and usage.

Consistent with the view expressed in Section 2, that there is a nearly continuous spectrum of possible engine designs, the opportunities for research will be discussed in a disciplinary breakdown of research areas. Estimates of the relative importance of the major research areas which have been identified, to the three main categories of engines, are given in Table 6-1.

In the discussion which follows, the research which can be expected to have large payoffs will be described and suggested objectives, approaches, and levels of effort will be given.

6.1 FLUID MECHANICS OF PISTON ENGINES

In most piston engine designs the shape of the flow passages and valves has been dictated largely by mechanical considerations, with the fluid mechanics a consequence and a secondary consideration. Although a good deal of empirical development has gone into the evolution of combustion volume shapes this has usually been within the constraints of a fixed engine layout, i.e., fixed valve sizes and positions, bore and stroke. It would appear that substantial improvements in both fuel economy and emissions can come from designs which are rationalized from the viewpoint of fluid mechanics. Indeed large improvements in performance have been obtained in engines

-46-

TABLE 6-1   ESTIMATES OF THE RELATIVE IMPORTANCE OF MAJOR RESEARCH AREAS

ENGINE RESEARCH AREA	DIESEL		STRATIFIED CHARGE		HOMOGENEOUS	
	Fuel Economy	Emissions	Fuel Economy	Emissions	Fuel Economy	Emissions
Fluid Mechanics	2	1	2	1	2	1
Chemical Kinetics	4	1	4	1	1	1
Liquid Fuel Injection Dynamics	2	1	2	1	4	4
Fuel Characteristics and Modifications	2	1	2	2	1	1
Cycle Modification-Forced Charging, Valve Control, etc.	2	3	1	1	1	3
Heat Loss Reduction	3	2	3	2	3	3

Key to Research Area Importance:

1   Very Important
2   Important
3   Possibly Important
4   Not Important

modified for racing purposes by relatively simple changes such as fairing and polish-
ing of inlet ports, tuning of inlet manifolds, etc. There is no reason why such refine-
ments cannot be incorporated into high production engines once optimized geometries
are known.

The importance of fluid mechanical refinement is probably greater in
Diesel engines and in stratified charge engines than in homogeneous spark
ignition engines. Both heterogeneous combustion engines have complex combustion
volume geometries which introduce losses and volumetric efficiency effects in addi-
tion to these found in the conventional Otto engine.

The opportunities here are conveniently divided into two groups, promising
improvements in fuel economy and emissions.

Fuel economy -- volumetric efficiency and pressure losses

The direct effects of fluid mechanical design on fuel economy are two. Fluid
friction losses reduce the useful work produced per unit of air flow, and so reduce
the thermal efficiency of the engine. The fluid friction also adversely influences
the volumetric efficiency of the engine. For a given swept volume and speed, the
efficiency of the engine improves as the volumetric efficiency is increased because
the mechanical friction is reduced relative to the output. Gas dynamic effects can
be exploited to improve the volumetric efficiency, particularly at high piston speeds,
so that high outputs can be attained from engines of small displacement, but unless
careful attention is paid to the friction losses thermal efficiency will be degraded
by the losses associated with high flow Mach numbers in valve ports.

In the heterogeneous combustion engines with prechambers or antechambers
significant losses in efficiency are associated with the expansion of the prechamber
fluid into the cylinder. In fact, this is the main reason for the low efficiency of the
prechamber Diesel (IDI) relative to the direct injection Diesel. While some such
loss is a necessary cost of mixing, no thorough geometrical and fluid mechanical
optimization has been carried out.

The fluid mechanics of viscous, unsteady flows of this sort is not well documented. An extensive and well coordinated program of theoretical, computational and experimental research will be required to produce the data base required for thorough optimization of designs.

To contribute to improvements in fuel consumption the program should thus include:

1. A systematic study of means for improving volumetric efficiency,

2. An evaluation of the effects of pressure loss on fuel economy, and

3. Development of a quantitative understanding of the relationship between pressure drop and turbulence level (see next section) in prechamber engines.

Emissions -- the effect of turbulence.

It is known that the rate of flame propagation and hence of heat release in homogeneous spark ignition engines is controlled by turbulent mixing, not by the laminar flame speed in the mixture. The most convincing proof of this is that the pressure rise occupies about the same crank angle independent of engine speed in an engine of fixed geometry.[2] The turbulent flame speed is proportional to the bulk gas velocity, which is in turn proportional to piston speed.

But there is a very large gap between understanding of such gross effects of turbulence and the kind of understanding which is required for modeling of the combustion process to predict pollutant formation. For this purpose, detailed knowledge of the turbulent mixing rate as a function of space and time during the cycle is necessary. More specifically, one would like to have the mean square intensity and energy spectrum of the turbulence at each point in the combustion volume during the compression and expansion processes.

A recent review has presented the state-of-knowledge of turbulence in spark-ignition engine.[73]   In this article, the turbulent velocity is defined as the fluctuation at a given crank angle, of the instantaneous velocity from an ensemble average of the velocities at the same geometrical point and crank angle for many strokes. This definition does not distinguish small scale fluctuations from the large scale flow during any particular stroke from stroke-to-stroke variations in the large scale flow. In fact, the data cited in Ref. (73) shows that during the intake and exhaust strokes the turbulent fluctuations are nearly equal in magnitude to the mean velocity, so it seems clear that stroke-to-stroke variations contribute largely to the "turbulence" as measured. Indeed, as Ref. (73) points out, Semenov[74] recognized that such results imply there is no mean flow at all.

It follows that the conventional understanding of turbulence, developed from study of flows behind screens, in shear layers and in turbulent boundary layers, will not be directly applicable to the problem of predicting mixing and combustion rates in piston engines. In these simpler situations, the turbulent fluctuations are supported by energy extracted due to instability of the mean flow, and the fluctuations are small compared to the mean flow velocity.

The conclusion that the "turbulence" in a piston engine is in part a stroke-to-stroke fluctuation of the large scale flow offers an explanation for the stroke-to-stroke variability in the combustion process, since it implies that the velocity over the spark plug of the homogeneous engine or over the injector of the stratified charge and Diesel engines, will vary from stroke to stroke. This may explain the random misfiring which sets the lean limit for spark ignition engines.[75]

There are many potential explanations for the stroke-to-stroke variability of the flow in piston engines. Vortex shedding from any bluff body in the flow passage, such as the inlet valve stem or head, is a random process which produces regions of vorticity with alternating signs. Similarly, separation processes at other points in the flow passages can have bistable character resulting in a randomness with respect to any particular stroke. It is a routine procedure in the development of high speed gas dynamic devices such as compressors, turbines, aircraft engine inlets and wings, to rationalize and control such flows so they are at least predictable, and it should be possible to do the same for piston engines.

When the mean flow has been stablized in this sense, it should then be possible to study it in detail to determine its actual turbulent structure in the conventional sense of fluctuations about a local mean which depends only on position and crank angle. This is the information required for a rational combustion system development.

To contribute to the reduction of emissions the program should thus include:

1. A detailed study of the sources of stroke-to-stroke variation of the large scale flow in the piston engine,

2. Development by modeling and experimental verification of techniques for stabilization of the large scale flow,

3. Detailed studies by modeling and by measurement of the turbulent and mean velocity structure of the stablized flow,

4. Development of means for tailoring the small scale turbulent structure to enhance mixing and control combustion.

In summary, it appears that a key to rational development of piston engines, especially Diesels and stratified charge engines, is the understanding of the fluid mechanical processes. More specifically, the flow in these engines must be made predictable, and invariant from stroke to stroke in regard to those factors which control the combustion process before a rational development can proceed.

<u>Recommended Research Program - Fluid Mechanics</u>

<u>Objectives</u>

1. To determine the sources of stroke-to-stroke variation of the large scale flows in piston engines of representative types, including: a typical spark-ignition homogeneous combustion engine, a typical prechamber type Diesel engine, and a typical stratified charge engine;

2. To evolve techniques for rendering the large scale flow in piston engines reproducible from stroke-to-stroke, so that at any geometrical point and any crank angle the flow fluctuation is small in magnitude and in scale, relative to the mean (over many strokes) flow;

-51-

3.   To determine the detailed turbulent structure of the stablized flow, in terms of mean square intensity, energy spectrum and scale, for representative spark ignition and Diesel engines;

4.   To develop means for tailoring the turbulent structure as required to provide mixing and cooling rates which are optimum from the standpoints of combustion efficiency and emissions reduction.

5.   To develop a quantitative understanding of the relationship between pressure drop and turbulence structure in prechamber engines.

6.   To develop rational means for improving the volumetric efficiency of piston engines.

Approach

A combination of theoretical, computational and experimental work is suggested. Theoretical work should be directed at the gas dynamics of the intake and exhaust processes and at modeling of viscous flows for incorporation in comprehensive numerical models of the intake, compression, power and exhaust processes. Computational efforts should address the modeling of the flow in the combustion volume, including the transfer from antechamber to cylinder in heterogeneous combustion engines. Experiments should enable detailed measurement of the flowfield throughout the intake, compression, expansion, and exhaust processes by optical or other methods and should be carried out in appropriately designed special apparatus rather than in engines. Direct comparison of local features of the flowfield with model predictions is essential to proper validation of the modeling.

Level of Effort

A substantial effort is recommended for this program element, which is regarded as key to the rational development of Diesel and stratified charge engines. A large experimental content will be necessary for success. A reasonable minimum level of effort for an academic or industrial research group is $150,000/year, and it would appear desirable to have two such groups attacking the flow definition problem for Diesels, and two for homogeneous and stratified spark ignition engines. All four groups should carry the program through the flow definition, refinement and turbulence study phases outlined above.   Such a program cannot be expected to yield definitive results in less than five years.

Thus, funding of $600,000/year over a period of five years for a total of $3M appears to be a minimum effort for this critical area. It may be desirable to increase the level at $1M/year after the first two years.

6.2 CHEMICAL REACTION MECHANISMS AND KINETICS

Overall, combustion in both spark ignition and Diesel engines is limited by mixing, not chemical kinetic processes. Therefore, no advance in chemical kinetic understanding is likely to significantly improve the fuel economy of conventional internal combustion engines.

However, exhaust emission levels from IC engines are greatly influenced by the finite rate nature of chemical reactions. Thus, increased understanding of reaction mechanisms and rate constants can lead to engine modifications designed to reduce pollutant emission levels.

As explained in Section 3, the detailed reaction kinetics which control both NO_x and CO emissions from internal combustion engines are well understood and characterized. The modified Zeldovich mechanism, clearly, controls NO formation, while hydroxyl radical oxidation is the major route for CO destruction. Adequate rate parameter data for combustion and exhaust temperatures and pressures are available for these processes. These data have already been incorporated into a number of engine models which can assess the effects of design changes on CO and NO_x emissions.[29,50,55,57,68] Any basic inadequacies in these models are due to incomplete fluid dynamic modeling rather than a lack of chemical kinetic data.

However, a major lack of kinetic data does exist for the pyrolysis and incomplete combustion of hydrocarbon fuels and lubricating oils. These processes lead to the federally regulated unburned hydrocarbon emissions in general, and to specific subclasses of objectional emissions such as soot, PAHs, aldehydes, olefins, light aromatics, and malodors. These emissions arise both from incomplete lubricating oil and fuel combustion in wall quench areas (spark ignition and Diesel engines) and from incomplete fuel combustion processes in both fuel rich and fuel lean zones associated with fuel sprays within heterogeneous combustors (Diesel and stratified charge engines). (See Subsection 3.5 for elaboration on these points).

-53-

While wall quench zones are accepted as being the major source of unburned hydrocarbon emissions in well tuned spark ignition engines,[50] the relative importance of the wall quench and fuel spray zones as sources of specific sub-classes of unburned hydrocarbon emissions is not completely clear. Thus, hydrocarbon pyrolysis and oxidation processes in both types of zones would benefit from further study. In general, both the rates of formation within the cylinder, and the rates of destruction within the cylinder and in the exhaust flow are unknown for for most classes of hydrocarbon emissions.

Key specific areas which suffer from incomplete reaction mechanism and rate parameter data include:

1. Fuel pyrolysis rates and products in both anoxic and partially oxiding regions;

2. Soot formation mechanisms and rates from fuel pyrolysis products.

3. Soot oxidation rates under cycle and exhaust conditions;

4. PAH formation rates from fuel pyrolysis products;

5. PAH gas phase degradation rates and mechanisms under cycle and exhaust conditions;

6. Rates of PAH and light aromatic adsorption, desorption and reaction with soot particles under late cycle and exhaust conditions;

7. Rates of PAH and light aromatic oxidation on soot particle surfaces under late cycle and exhaust conditions;

8. Rates of gas phase formation and oxidation of light aromatics, aldehydes and olefins under cycle and exhaust conditions;

9) Rates of gas phase formation and destruction of malodors under cycle and exhaust conditions;

10) Rates and mechanisms of malodor adsorption, desorption and reaction with soot particulates under late cycle and exhaust conditions.

Since the unburned hydrocarbon emissions problem is much more serious for Diesel and stratified charge engines than for conventional spark ignition engines, the research program outlined below concentrates on research opportunities designed for such systems.

Recommended Research Program - Chemical Kinetics

Objectives

To determine the mechanisms and rates of production of various classes of unregulated emission arising from incomplete hydrocarbon combustion in stratified charge and Diesel engines, to design engine modifications to alleviate these emissions, and to assess the impact on fuel consumption of these modifications. The classes of emissions to be considered include soot, polycyclic aromatic hydrocarbon compounds (PAH, both gas phase and absorbed on exhaust particulates), aldehydes and odor producing hydrocarbons and oxyhydrocarbons.

Approach

1. The relative importance of lubricating oil consumption and incomplete fuel combustion as sources of these emissions will be examined by means of engine tests with controlled oil and fuel consumption.

2. The mechanisms by which lubricating oil consumption and fuel combustion each contribute to the emissions will be examined by a combination of theoretical modeling and fundamental experimentation. Experimental approaches to the study of the production mechanisms should enable detailed examination of the physical and chemical aspects of pollutant production including droplet size and spatial distribution, droplet vaporization rates, soot formation, concentration of polycyclic aromatic hydrocarbons, aldehydes, light aromatics, olefins, malodors, and others as are pertinent. Steady flow or single event analogues which maximize diagnostic possibilities are preferred over engine tests, but the fluid mechanics and chemical kinetics of the critical portions of the engine combustion process must be accurately modeled.

3. Based on the results of 1) and 2), engine modifications to reduce the pollutant emissions will be projected. Their impact on currently regulated emissions (NO_x, CO, and unburned hydrocarbons) and on fuel consumption will be estimated. Selected engine modifications will then be evaluated by engine testing.

Suggested Tasks

1. Perform experimental studies on automotive Diesel engines to determine the relative contributions of incomplete fuel combustion and lubricating oil consumption.

and degradation on emissions of polycyclic aromatic hydrocarbons, aldehydes, soot and odorous compounds. Light duty and heavy duty precombustion chamber and direct injection engines are to be used as test vehicles, with driving cycle appropriate to each. Well characterized and homogeneous stocks of representative fuels and oils will be needed to perform this task. State-of-the-art exhaust dilution, sampling and analysis procedures will be necessary. Particular attention should be paid to complete PAH analysis.

2. Determine the relative contributions to particulate, aldehyde, PAH, and odorous emissions of the various constituents of lubrication oils, by engine testing of oils with varied composition and additives. Particular attention to exhaust characterization, including complete PAH analysis will be required for this task.

3. Experimentally and theoretically model the fluid mechanical, thermal and chemical behavior of lubricating oil exposed on cylinder walls to the combustion gases, to determine the products of decomposition.

4. Determine experimentally the conditions under which soot, aldehyde, PAH, and odorous compounds are produced in the heterogeneous combustion processes of Diesel engines. Diagnostics must be adequate to establish the connection between the rate of production of pollutants or their precursours and pressure, temperature and composition of the mixture at each point in the engine cycle. Single event time resolved measurements or measurements in steady flows simulating single points in the engine cycle are preferred over engine tests. Optical or other in situ techniques should be considered for droplet and soot measurements. Sampling will be acceptable for PAH, aldehydes and odorous emissions if characteristics of sampling devices are established.

5. Model the production of PAH, soot, aldehydes and odorous emissions in the heterogeneous combustion process of Diesel engines, placing emphasis on determining the parametric changes which will reduce such emissions. Estimate theoretically the impact of such parametric changes on fuel consumption and engine performance.

6. Design, fabricate, test and evaluate engine designs selected to minimize emissions of odorous, soot, aldehyde and PAH compounds as well as regulated pollutants, while maintaining or improving current Diesel fuel economy and durability.

Level of Effort

The level of effort needed to achieve the objectives outline in this subsection is substantial. Suggested funding levels and time phasings for each task are shown in the table below.

SUGGESTED TIMING AND FUNDING LEVELS
FOR CHEMICAL KINETIC TASKS

TASK \ YEAR	1	2	3	4	5
1) Importance Of Oil Consumption Vs. Fuel Combustion As Source Of Unregulated Emissions (Engine Tests) 1 Contract	200				
2) Analysis Of Oil Characteristics Which Influence Unregulated Emissions (Engine Tests) 1 Contract		200	200		
3) Modeling Of Effects Of Oil Decomposition and Consumption On Unregulated Emissions 1 Contract		200	200		
4) Experimental Determination Of Mechanisms For Unregulated Emissions Production From Incomplete Fuel Combustion 2 Contracts	600	600	500	500	200
5) Modeling Of Unregulated Emission Production From Incomplete Fuel Combustion 2 Contracts	200	200	300	300	200
6) Engine Modification Design And Evaluation 2 Contracts			200	600	1000
TOTALS: $K	1000	1200	1400	1400	1400

6.3 LIQUID FUEL INJECTION DYNAMICS AND SPRAY COMBUSTION

Precise control of the fuel injection process is critical to the full exploitation of the advantages of both the Diesel and all stratified charge engines which use in-cylinder fuel injectors. The fuel must be injected at the right time in the cycle, to control the pressure-time heating and assure complete combustion without making an undue roughness. The fuel must be injected so as to properly mix with the air. These requirements have, in the past, been met for Diesels by a long process of empirical development. With the new concerns about particulate emissions and the different requirements of stratified charge engines, it seems that an intensive theoretical and experimental program of research on the dynamics of fuel delivery and injection is in order.

There are several elements to the problem, namely:

1.   Fuel pressurization and metering,
2.   Fuel spray formation, and
3.   Spray combustion,

of which the first two have to do with the hydrodynamics and mechanics of the fuel supply system, the second deals with the spray formation, and the last includes the complex processes of droplet vaporization and turbulent combustion of the resultant fuel vapor. They will be discussed in that order.

6.3.1 Fuel Pressurization and Metering

The design objective in the fuel supply system is to deliver fuel to the injection nozzles at the right pressure and to schedule the injection orifice area so as to produce the desired flow rate and injection pattern as a function of crank angle. The fuel system may use unit injectors, individual remote pumps or a distributor pump; in the latter two cases, the nozzles open in response to fuel pressure provided by pumps through rather long tubing, and hydroelastic wave phenomena in these lines can cause delays in injection and after injection. In all cases, the dynamics of the injection valve itself can cause after injection when the valve bounces open after the intended termination of the injection.[29] This phenomenon can be a major source of smoke particulates and odors, since it causes injection with low pressures, late in the cycle.

Although the dynamics of injection systems has been studied extensively and is well understood in principle,[1, 2] it is complex enough that the behavior of any actual fuel system differs significantly from the ideal. With the more stringent requirements likely to be imposed by particulate and odor control it will be necessary to develop more precise models for fuel system behavior. Modern computational capabilities should make this feasible now, whereas, in the past sheer complexity limited the precision with which the fuel system behavior could be treated.

Accordingly, it is recommended that a capability be developed for comprehensive numerical modeling of fuel system dynamics. Models should be developed for each of the popular systems, using remote individual or distributor pumps and unit injectors. They should model accurately, the fluid mechanics and structural dynamics of the pumps, links, and injection nozzles, and should be validated by critical experiments.

6.3.2 Spray Formation

Existing injection systems for Diesel and stratified charge engines introduce the fuel in sprays, the atomization of which is controlled by the shape of the nozzle and the pressure drop across it. The velocity and turbulence level of the airflow over the nozzle also play an important role in overall behavior. In the development of nozzles for gas turbine combustors, a painstaking process of empirical refinement of the airflow and nozzle design is required to achieve acceptable combustor performance. To achieve comparable results for piston engines, it appears an equivalent process is necessary, but the problem is more difficult because of the variation with crank angle of the fuel pressure, nozzle opening, and airflow.

In the spirit of the discussion of fluid mechanics of Subsection 6.1, a full rationalization of the fuel spray behavior will be necessary to achieve the potential of the Diesel and stratified charge engines for emissions control and fuel economy. This means the fuel spray behavior must be understood at each crank angle for every load condition. When the fluid mechanics are understood as outlined in 6.1 and the fuel system behavior as indicated in 6.3.1, it should be possible to study the

spray behavior at each crank angle and load condition by means of <u>steady state</u> experiments. By a process of iteration, it should then be possible to refine the fluid mechanical design and fuel system design so as to produce the desired spray characteristics.

What is recommended then, is the development of capability for studying experimentally the <u>steady state</u> characteristics of spray formation by representative nozzle designs, for pressure, flow rates, and airflow conditions representative of all important operating conditions for Diesel and stratified charge engines.

6.3.3 <u>Spray Combustion</u>

After the fuel spray enters the combustion volume, the fuel vaporizes, mixes with the air to form a locally near stoichiometric mixture, reacts and may then be diluted and cooled by mixture with excess air. The recent literature [76, 77, 78, 79] indicates that the classical concept of a single burning droplet surrounded by a flame front is not applicable to most practical combustors. Rather, the fuel spray evaporates to form a cloud of fuel vapor, which is then mixed with the air and combusted at a rate largely controlled by turbulent mixing. In this picture, the character of the turbulent flow controls the combustion rate and the cooling rate, hence, the formation of unburned hydrocarbons, NO_x and soot.

Again, a full rationalization of the combustion process depends on understanding the turbulent combustion at each crank angle and load. And, given the understanding of the fluid mechanics projected in Subsection 6.1, this can be achieved by a series of steady state experiments which represent the critical operating points. The advantage of steady state experiments is that they will enable the use of the type of sophisticated measurement techniques required to determine the locations in the combustion zone, where the particulates, NO_x and odorous substances are formed. This should make possible a systematic reduction of the pollutants by tailoring the spray pattern and turbulence.

Recommended Research Program – Injection Dynamics and Spray Combustion

Objectives

1.   To develop accurate numerical models of fuel delivery systems for Diesel and stratified charge engines.

2.   To develop a capability for experimentally defining spray characteristics of representative injectors as a function of airflow pattern, injector pressure drop and nozzle geometry.

3.   To determine the locations where pollutants are formed and the mechanisms of their formation in spray combustion systems for Diesel and stratified charge engines.

4.   To evolve by a systematic experimental and analytical process, means for prediction, and reducing pollutant emissions in heterogeneous combustion systems.

Approach

1.   A combination of numerical modeling by digital computation and verification by critical experiments is suggested for rationalization of the fuel system dynamics. The modeling should be comprehensive enough to encompass all fuel delivery systems which appear to be promising, including unit injectors, remote individual pumps and distributor pumps.

2.   An approach through steady flow experiments is recommended, the parameters of the experimental being variable so as to simulate accurately all critical operating points for the engine. The airflow pattern, and fluid mechanical parameters and geometry should all be modeled correctly in a dimensionless sense. Modern nonintrusive techniques should be used where possible to map the flow and determine droplet distributions.

3.   Steady flow spray combustion experiments should be performed which model each of the critical operating conditions of crank angle and load. Detailed measurements of temperature and species concentrations should be carried out throughout the spray combustion zone, by sampling or by optical techniques where possible.

4.   Based on the results of (1), (2), (3), the spray pattern and airflow should
be modified so as to reduce pollutant formation, and the results should then be
assessed experimentally.   Whenever possible,this experimental process should be
supported by analytical and numerical modeling.

Level of Effort

Fuel System Dynamics - 2 contracts - $100,000/yr. for 3 yrs.

Spray Formation - 2 contracts - $200,000/yr. for 3 yrs.

Spray Combustion - 2 contracts - $300,000/yr. for 5 yrs.

6.4 FUEL CHARACTERISTICS AND MODIFICATIONS

Fuel characteristics can influence exhaust emissions either because fuels contain additives or impurities which are exhausted as objectional species, or because their combustion characteristics are not suited to engine conditions and incomplete burning results. This later phenomena can also adversely impact fuel economy.

As discussed in subsection 3.2.2, fuel additives and impurities can lead directly to objectionable emissions. Emissions of this type include: a) lead particulates from tetralkyl lead compounds added to gasoline as antiknock agents; b) SO_2 and sulfate particulates due to sulfur in gasoline and Diesel fuel; and c) excess non-Zeldovich NO_x due to the oxidation of nitrogen containing fuel additives. As noted in subsection 2.8, the best way to control these "garbage in-garbage out" pollutants is to restrict their input levels in the fuel so that nonobjectionable output levels. This procedure is illustrated by federal regulation of sulfur and lead alkyl levels in automotive fuels.

A less understood, but potentially more rewarding topic for research effort involves the influence of fuel content on combustion efficiency and the production of specific classes of unburned hydrocarbon emissions. A case in point is the observation that increased light aromatic content in fuels leads to increased PAH concentrations in the exhaust[20, 21]. Unfortunately there are relatively few reliable measurements of the influence of fuel composition on specific unburned hydrocarbon emissions such as soot, PAH's, malodors, aldehydes and light aromatics, particularly for Diesel systems.

A research program which involves precombustion characterization of prototype fuels of nearly equivalent centane number, but varying compositions, followed by careful exhaust measurements which quantified each of the hydrocarbon emission classes could illustrate the impact of fuel composition on various types of hydrocarbon emissions in heterogeneous combustion systems. Accurate and reliable analytical techniques for each major unburned hydrocarbon class must be demonstrated. The simultaneous measurement of each major emission class is recommended, since reductions in one class may be accompanied by increases in an equally objectionable second class.

-63-

The actual combustion tests would be run on both a laboratory combustion device which simulates Diesel cylinder conditions, as described in Subsection 6.1.1, and in prototype engines. Initial work with laboratory scale devices is particularly suited for demonstrating the capability of the analytical methods chosen to characterize the exhaust pollutant levels.

Recommended Research Program – Fuel Characterization and Modification

Objectives

To determine the influence of fuel composition on combustion efficiency and exhaust emission levels for unburned hydrocarbon classes including soot, PAHs, light aromatics, aldehydes and malodors.

Approach

1. Various synthetic or commercially-produced fuels of comparable cetane number will be characterized and classified according to composition. These fuels should exhibit significant variations in aromatic, olefinic and branched chain composition.

2. The fuels characterized in Step 1 shall be burned, first under laboratory simulated Diesel engine conditions, and then in prototype Diesel engines, under a variety of stoichiometric conditions. The exhausts from those tests will be accurately analyzed for soot, PAH, malodor, light aromatic, and other unburned hydrocarbon levels.

3. Correlations between fuel composition and emissions of various classes of unburned hydrocarbon will be examined and confirmed.

4. Recommendations about federal regulation of Diesel fuel composition will be prepared.

Level of Effort

Preparation and Characterization of Test Fuels – $75,000/yr. for 1 yr.

Development of Exhaust Analysis Techniques – $75,000/yr. for 2 to 3 yr. programs

Laboratory Simulation Combustion Tests – $75,000/yr. for 2 yrs.

Engine Combustion Tests – $75,000/yr. for 2 yrs.

Data Analysis and Preparation of
Regulatory Recommendations   – $50,000/yr. for 2 yrs.

6.5 CYCLE MODIFICATION

Any of the three basic engine types, homogeneous spark ignition, Diesel and stratified charge can be modified in many ways to improve its maximum output or its part load fuel economy or both. Some of these possibilities have been explored in the past, but future constraints on fuel consumption necessitate a new and more rigorous examination of these alternatives. Some which should be thoroughly evaluated are; geared and exhaust turbine driven superchargers, valve control to achieve part load operation, variable compression ratio in Diesels. We will discuss each briefly.

6.5.1 Supercharging

The full throttle power, of a normally aspirated piston engine is roughly proportional to speed, while the power requirement of an automobile increases somewhere between the square and the cube of the speed, so unusual transmission arrangements aside, the engine operates at very light loads at usual vehicle speeds.

A geared supercharger produces an inlet manifold pressure boost which is about proportional to speed squared, so would, if appropriately sized, cause the engine full throttle power to vary as speed squared. It would boost the manifold pressure at high engine speeds irrespective of engine load. The turbosupercharger has the further advantage that its boost increases as engine load is increased at any speed because of the increase of exhaust gas pressure at high throttle settings. Thus, particularly with a turbosupercharger an engine of smaller displacement can be used for any given vehicle.

As is pointed out in Ref (2), supercharging results in an increase in fuel consumption at full load because of the decrease in compression ratio required if the engine is knock limited. Thus, if the lower function of the smaller engine is to result in an overall decrease in fuel consuption, it may be necessary to combine supercharging with some way of varying the compression ratio so it can be low at full power when the engine is supercharged and high at part power where fuel consumption is most critical.

In spite of its obvious performance advantages, the turbosupercharger has not seen wide application on automobiles, because of its cost and this will remain a problem. Higher production quantities would help, but the high speed bearings, stress, and

temperature requirements in the turbine are basic cost generating problems. It would appear that effort should be concentrated on these aspects of turbosupercharger technology, especially on the development of techniques for design and fabrication of ceramic (silicon nitride) hot parts.

In the application of ceramics to gas turbines, their brittleness is a key problem in that it leads to a lack of defect tolerance. Generally, ceramic parts for turbines have been fabricated to the same geometric requirements as the original metal parts which they have been meant to replace. It has been argued[80] that is a mistaken approach and that the different mechanical characteristics of the ceramics should be accounted for in the original design even to the extent of somewhat compromising the fluid mechanical design. Thus, a coordinated program of turbomachine design and testing and ceramic fabrication work is called for.

A thorough study should be made of the potential gains in fuel consumption from turbosupercharging before a large program commitment is made.

Recommended Research Program - Supercharging

Objectives

1. To assess the gain in fuel consumption which would result from large scale use of turbosuperchargers with compression ratio control in automobiles.

2. To develop design procedures, materials and manufacturing techniques for ceramic hot parts for automotive turbosuperchargers.

Approach

A cost/benefit analysis of the potential fuel savings required to determine whether the major investment required to develop ceramic technology for large scale application can be justified. If the answer is affirmative, the approach should be to develop turbosupercharger designs which make best use of ceramic materials, and are acceptable from the viewpoint of gasdynamics.

Level of Effort

Assessment - \$50,000/yr. - 1 yr.

Ceramic fabrication and materials development - 2 contracts - \$3000,00/yr.
for 3 yrs.

Turbine design - 2 contracts - \$200,000/yr for 2 yrs.

-66-

6.5.2 Valve Control

A currently produced example of valve control is the Eaton Valve Selector[81] which simply deactivates the intake and exhaust valves of one or more cylinders when less power is needed, eliminating their pumping losses and raising the load of the remaining cylinders to a more efficient level.

There are many possibilities for use of such techniques to vary the effective displacement and compression ratio so as to more optimally match starting and part load requirements. For example, a higher compression ratio is required for starting and idling Diesel engines than is desired for optimum full load fuel economy and performance. Delayed closing of the intake valve under high load conditions would lower the effective compression ratio but at the same time reduce the volumetric efficiency. A higher compression ratio is also possible in homogeneous and stratified charge engines at throttled conditions if the limit is set by pre-ignition, and again such a change could be implemented by valve control.

Recommended Research Program - Valve Control

Approach

It appears that a systematic theoretical study of the potential fuel savings and emissions reductions which can be realized by such changes in valve operation is in order as a first step. When promising changes have been identified, detailed mechanization, cost and durability studies should be initiated.

Level of Effort

Theoretical studies - $50,000/yr - 1 yr.

Mechanization and design studies - contingent on results of theoretical work

6.6 HEAT LOSS REDUCTION

Heat losses to the cooling system and oil account for about one-third of the total energy input to a typical spark ignition engine. These losses are distributed roughly as indicated in the following table:[1]

Process	Heat Loss %	Available Loss %
Compression	0.5	0.07
Combustion	7.0	2.51
Expansion	9.0	1.29
Exhaust	17.0	0

which shows the heat loss in percent, and the recoverable portion of it, i.e., the increase in work which would occur if the loss did not occur. Because so much of the heat loss occurs in the expansion process and in flow through the exhaust ports only about one-tenth of the heat loss is recoverable. The values differ somewhat for a Diesel engine, but not enough to change the overall conclusion, which is that reduction of heat losses from a piston engine, by insulation of the piston or cylinder will not in itself make appreciable changes in fuel consumption.

The potential of the "adiabatic engine", such as, is described in Ref. (82) stems from the possibility of recovery of energy from the exhaust gases by means of a exhaust gas turbine geared to the crankshaft. In this case, the expansion and exhaust cooling losses become partially recoverable, and substantial gains are predicted from insulation of the piston, cylinder and exhaust manifold.

This concept promises substantial gains in fuel economy only at high load conditions, where the pressure at release is high, hence, it does not seem promising for automotive applications, insofar as reduction of fuel consumption is concerned. It may be that hot piston, cylinder and exhaust surfaces could

radically reduce CO and HC emissions due to quench, but it seems doubtful that the very difficult technology of the "adiabatic engine" could compete with exhaust gas treatment by catalysis or by a thermal reactor. For this reason, no research on heat loss reduction will be recommended.

7. SUMMARY

The ability of heterogeneous combustion systems, such as, Diesel and stratified charge engines to operate under very lean burn conditions provides these systems with a major theoretical cycle efficiency advantage due primarily to their achievement of a low heat capacity working fluid. This effect contributes substantially to the part load fuel economy advantage which Diesel engines exhibit over conventional spark ignition engines. The same principle will apply to stratified charge engines.

Furthermore, these same lean burn conditions lead to lower overall in-cylinder gas temperatures, thus minimizing NO_x production.

Thus, two major potential benefits, higher fuel economy and lower NO_x emissions, would seem to strongly bias future research and development efforts for light duty vehicle engines in favor of heterogeneous (Diesel or stratified charge) engines.

However, these potential benefits must be weighed against the fact that current models of heterogeneous systems produce high levels of exhaust emissions due to incompletely combusted fuel (and lubricating oil). These emissions include carbon monoxide (CO), soot, polycyclic aromatic hydrocarbons (PAHs), malodors, light aromatics, and aldehydes. Each of these emission types posed potentially serious health or environmental problems. CO is toxic at high levels and leads to cardiovascular stress at lower levels. Soot is produced primarily in submicron respirable particles which directly irritate lung tissue as well as convey harmful absorbed chemicals into the throat and lungs. Many PAHs and related aromatic compounds are suspected human carcinogens. Exhaust malodors are at best unpleasant and nauseating, and aldehydes and other light incompletely burned hydrocarbons are key precursors of photochemical smog.

No fundamental principal requires that heterogenous combustion systems produce high emission levels due to incompletely combusted fuel. Since these engines are customarily operated lean, they have the theoretical capability of completely oxidizing all fuel (and entrained lubricating oil) to carbon dioxide and water. The challenge is to achieve more nearly in practice, the complete fuel oxidation chemistry that is theoretically possible.

It seems clear that the major impediment to controlling and improving CO and incompletely burned hydrocarbon emission levels is the lack of understanding of the fluid mixing processes which control combustion in heterogeneous systems. Engine measurements, made to date, indicate that not only are these mixing processes not understood, they are not even repeatable from cycle to cycle. Thus, the most important tasks in domesticating heterogeneous combustion engines are: first, the control, and second, the prediction of the fluid mixing processes during the stroke. This rationalization of the combustion fluid mechanics would provide a basis for specification of the chemical conditions necessary to eliminate CO and hydrocarbon emissions without increasing NO_x or sacrificing fuel economy.

A second set of challenges involves the elucidation of chemical mechanisms and rates which control the formation and destruction of complex incompletely burned emissions, such as, soot, PAHs, or malodors. The details of soot or PAH formation in even a simple laboratory flame are not known. Even less is known about their formation under conditions typical of piston engines. It seems clear that detailed experimental and theoretical work will be necessary before these processes are understood at the level necessary for their elimination.

After rationalization of the fluid mixing processes is obtained and the complex hydrocarbon emission chemistry is determined, detailed modeling of exhaust emissions and fuel efficiency in heterogeneous engines will be possible. These

models should include NO_x and CO emission chemistry, which is presently known in detail along with soot, PAH, maloder, and other currently unregulated emissions. The ability to model, and thus, predict the effect of engine modifications on fuel economy and both regulated and unregulated emissions is the key to the systematic and rational development of heterogeneous engines as efficient and environmentally sound, light duty vehicle propulsion sources.

Rationalization of the fluid mechanics could also lead to major improvements in the emissions and fuel economy of homogeneous spark ignition engines by minimizing the stroke-to-stroke variability which presently fixes the combustion lean limit by causing misfiring.

A suggested research and development program designed to achieve the experimental data and analytical models necessary to perform these tasks is presented in Section 6 of this report. A summary of the total recommended research program, including suggested levels of effort, is contained in Table 7-1.

TABLE 7-1 SUMMARY OF RECOMMENDED RESEARCH PROGRAMS

Research Topic/Task	Number of Contracts	Duration of Contracts (yrs.)	Total Level of Effort ($K/yr.)	Total Expenditure Over Program ($K)
1. Fluid Mechanics				
a. Rationalization of Engine Fluid Mechanics	2 (Spark Ignition Engines) 2 (Diesel Engines)	5 (each)	600 to 1000	3000 to 4200
2. Chemical Kinetics and Mechanisms				
a. Emissions vs. Oil Consumption Engine Meas.	1	1	200	200
b. Emissions vs. Oil Characteristics Engine Meas.	1	2	200	400
c. Oil Decomposition Modeling	1	2	200	400
d. Experimental Studies of Unregulated HC Emissions Chemistry	2	5	200 to 600	2400
e. Modeling of Unregulated HC Emissions	2	5	200 to 300	1200
f. Engine Modification Design and Evaluation	2	3	100 to 500	1800

TABLE 7-1   SUMMARY OF RECOMMENDED RESEARCH PROGRAMS (Cont.)

Research Topic/Task	Number of Contracts	Duration of Contracts (yrs.)	Total Level of Effort ($K/yr.)	Total Expenditure Over Program ($K)
3. Fuel Injection and Spray Combustion				
a. Fuel Injection Dynamics Studies	2	3	100	300
b. Spray Formation Studies	2	5	200	1000
c. Spray Combustion Studies	2	5	300	1500
4. Fuel Characteristics and Modifications				
a. Preparation and Characterization of Test Fuels	1	1	75	75
b. Development of Exhaust Analysis Techniques	2 to 3	2	150 to 225	300 to 450
c. Laboratory Simulation Tests	1	2	75	150
d. Engine Tests	1	2	75	150
e. Data Analysis and Recommendations	1	2	50	100

TABLE 7-1   SUMMARY OF RECOMMENDED RESEARCH PROGRAMS (Cont.)

Research Topic/Task	Number of Contracts	Duration of Contracts (yrs.)	Total Level of Effort ($K/yr.)	Total Expenditure Over Program ($K)
5. Cycle Modification				
a. Supercharging Assessment Studies	1	1	50	50
b. Ceramic Materials Development	2	3	600	1800
c. Turbine Design Studies	2	2	400	800
d. Valve Control Assessment	1	1	50	50
e. Valve Mechanization	---------------- Contingent on 5a ----------------			
Program Totals	~30	1 to 5	~3000	~16000

APPENDIX A

REFERENCES

1. Lichtz, L.C., Internal Combustion Engines, McGraw-Hill (1951).

2. Taylor, C.F., The Internal Combustion Engine in Theory and Practice, Vol. I and II, MIT Press (1960).

3. Austin, T.C. and McFadden, J.J., "A Study of Stratified Charge for Light-Duty Power Plants," Vol. I, Ricardo & Co., EPA-460/374-011A (October 1975).

4. Inoue, K., Ukawa, H., Fujii, I., "Fuel Economy and Exhaust Emissions of the Honda CVCC Engine," Combustion Science and Technology, Vol. 12, pp. 11 - 27 (1976).

5. Mitchell, E. and Alperstein, M., "Texaco Controlled-Combustion System - Multifuel, Efficient, Clean, and Practical," Combustion Science and Technology, Vol. 8, pp. 39 - 49 (1973).

6. Miyake, M., Okada, S., Kawahara, Y., and Asai, K., "A New Stratified Charge Combustion System (MCP) for Reducing Exhaust Emissions," Combustion Science and Technology, pp. 29 - 46 (1976).

7. Leighton, P.A. Photochemistry of Air Pollution, Academic Press, New York, N.Y. (1961)

8. Niki, H., Daby, E.E., and Weinstock, B., "Photochemical Smog and Ozone Reactions," Adv. Chem., 113, 16 (1972).

9. Hecht, T.A., Seinfeld, J.H., and Dodge, M.C., "Further Development of Generalized Kinetic Mechanics for Photochemical Smog," Envir. Sci. & Tech., 8, 327 (1974).

10. Calvert, J.G., "Hydrocarbon Involvement in Photochemical Smog Formation in Los Angeles Atmosphere," Envir. Sci. & Tech., 10, 256 (1976).

11. Chameodes, W.L. and Walker, J.C.G., "A Time-Dependent Photochemical Model for Ozone Near the Ground," J. Geophys. Res., 81, 413 (1976).

12. Fishman, J. and Crutzen, P.J., "A Numerical Study of Tropospheric Photochemistry Using a One-Dimensional Model," J. Geophys. Res., 82, 5897 (1977).

References (Cont.)

13. Johnston, H.S., "Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhausts," Science, 173, 517 (1971).

14. "The Effects of Stratospheric Pollution by Aircraft," Final Report of the CIAP Program, Department of Transportation, Washington, D.C. (December 1974).

15. Calvert, J.G., "Test of the Theory of Ozone Generation in Los Angeles Atmosphere," Envir. Sci. & Tech., 10, 248 (1976).

16. Vuk, C.T., Jones, M.A., and Johnson, J.H., "The Measurement and Analysis of the Physical Character of Diesel Particulate Emissions," SAE Transactions, Paper No. 760131, 556 (1976).

17. Laresgoiti, A., Loos, A.C., and Springer, G.S., "Particulate and Smoke Emission from a Light-Duty Diesel Engine," Envir. Sci. & Tech., 11, 973 (1977).

18. Spindt, R.S., "Second Year Report on Polynuclear Aromatic Content of Heavy Duty Diesel Engine Exhaust Gases," Gulf Research and Development Co., Pittsburgh, Pennsylvania (January 1977).

19. Gross, G.P., "The Effect of Fuel and Vehicle Variables on Polynuclear Aromatic Hydrocarbon and Phenol Emissions," SAE, Paper No. 720210, (1972).

20. Newhall, H.K., Jetoft, R.E., and Ballinger, P.R., "The Effect of Unleaded Gasoline Composition on Polynuclear Aromatic Hydrocarbon Emissions," SAE, Paper No. 730834, (1973).

21. Zughini, N., Menglini, S., Arteconi, M., and Sezzi, F., "Polynuclear Aromatic Hydrocarbons in Vehicle Exhaust," SAE, Paper No. 7308361.

22. Blumer, M., Blumer, W., and Reich, T., "Polycyclic Aromatic Hydrocarbons in Soils of a Mountain Valley: Correlation with Highway Traffic and Cancer Incidence," Envir. Sci. & Tech., 12, 1082 (1977).

23. Gage, S., "Precautionary Notice on Laboratory Handling of Exhaust Products from Diesel Engines," EPA Memo (November 1977).

24. Spindt, R.S., Barnes, G.J., and Somers, J.H., "The Characterization of Odor Components in Diesel Exhaust Gas," SAE, Paper No. 710605 (1971).

25. "Chemical Identification of the Odor Components in Diesel Engine Exhaust," Arthur D. Little, Inc., Final Report to CRC and NAPCA, CRC Project CAPE-7-68, HEW Contract No. CPA-22-69-63 (June 1970).

References (Cont.)

26. Somers, J.H., and Kittridge, G.D., "Review of Federally-Sponsored Research on Diesel Exhaust Odors," Report No. 71-75, EPA, Ann Arbor, Michigan (July 1971).

27. Levins, P.L., Kendall, D.A., Caragay, A.G., Leonardos, G., and Oberholtzer, J.E., "Chemical Analysis of Diesel Exhaust Odor Species," SAE, Paper No. 740216, SAE Transations, 949 (1974).

28. Springer, K.J., "Investigations of Diesel-Powered Vehicle Emissions VII," EPA Publication, No. EPA-460/3-76-034 (February 1977).

29. Henein, N.A., "Analysis of Pollutant Formation and Control and Fuel Economy in Diesel Engines," Prog. Energy Comb. Sci., 1, 165 (1976).

30. Patterson, D.J. and Henein, N.A., Emissions from Combustion Engines and Their Control, Ann Arbor Science, Ann Arbor, Michigan (1972).

31. Darnall, K.R., Lloyd, A.C., Winer, A.M., and Pitts, J.H., Jr., "Reactivity Scale for Atmospheric Hydrocarbons Based on Reaction with Hydroxyl Radical," Envir. Sci. & Tech., 10, 692 (1976).

32. Keeling, C.D. and Rotty, R.M., "The Global Carbon Dioxide Problem," Baes, C.F., et al., Eds., Report No. ORNL-5194, Dept. of Commerce, Washington, D.C. p. 18 (1976).

33. Stuiver, M., "Atmospheric Carbon Dioxide and Carbon Reservoir Changes," Science, 197, 253 (1978).

34. Woodall, G., et al., "The Biota and the World Carbon Budget," Science, 199, 14 (1978).

35. Mercer, J.H., "West Anartic Ice Sheet and CO_2 Greenhouse Effect: A Threat of Disaster," Nature, 271, 321 (1978).

36. McElroy, M.B. and McConnel, J.C., "Nitrous Oxide: A Natural Source of Stratospheric NO," J. Atmos. Sci., 28, 1095 (1971).

37. McElroy, M.B., Wofsy, S.C., and Yung, Y.L., "The Nitrogen Cycle: Perturbations Due to Man and Their Impact on Atmospheric N_2O and O_3," Phili. Trans. Roy. Soc., 277B, 159 (1977).

38. Wang, W.C., Yung, Y.L. Lucis, A.A., Mo, T., and Hansen, J.E., "Greenhouse Effects Due to Man-made Perturbations of Trace Gases," Science, 194, 685 (1976).

References (Cont.)

39. Weiss, R.F. and Craig, H., "Production of Atmospheric Nitrous Oxide by Combustion," Geophys. Res. Lett., 3, 751 (1976).

40. Pierotti, D. and Rasmussen, R.A., "Combustion As a Source of Nitrous Oxide in the Atmosphere," Geophys. Res. Lett., 2, 265 (1976).

41. Elkins, J.W., Kolb, C.E., and Wofsy, S.C., Unpublished results.

42. Kaplan, W.A., Elkins, J.W., Kolb, C.E., McElroy, M.B., Wofsy, S.C., and Duran, A.P., "Nitrous Oxide in Fresh Water Systems: An Estimate for the Yield of Atmospheric N_2O Associated with Disposal of Human Waste," Pure Appl. Geophys., in press.

43. Esser, J. and Laidler, K.J., "The Pyrolysis of Ethane in the Presence of Nitric Oxide," Int. J. Chem. Kinet., 2, 37 (1970).

44. Schuchmann, H.P. and Laidler, K.J., "The Pyrolysis of Acetaldehyde in the Presence of Nitric Oxide," Int. J. Chem. Kinet., 2, 349 (1970).

45. Fenimore, C.P., "Formation of Nitric Oxide in Premixed Hydrocarbon Flames," Thirteenth Symposium (International) on Combustion, p. 373, The Combustion Institute, (1971).

46. Iverach, D., Basden, K.S., and Kirov, N.Y., "Formation of Nitric Oxide in Fuel-Lean and Fuel-Rich Flames," Fourteenth Symposium (International) on Combustion, p. 767, The Combustion Institute (1973).

47. Schuchmann, H.P. and Laidler, K.J., "Nitrogen Compounds Other Than NO in Automobile Exhaust Gas," J. Air. Pollut. Cont. Assoc., 22, 52 (1972).

48. Myerson, A.L. and Blair, D.W., "Reduction of Nitric Oxide in Automobile Engine Exhaust by Ethane-Air Injection," Envir. Sci. & Tech., 10, 461 (1976).

49. Somers, J.H., EPA Office of Mobile Source Emission Control, Research Triangle Park, NC - Private Communication.

50. Heywood, J.B., "Pollutant Formation and Control in Spark-Ignition Engines," Prog. Engr. Comb. Sci., 1, 135 (1976).

51. Cadle, S.H., Chock, D.P., Monson, P.R., and Heuss, J.M., "General Motors Sulfate Dispersion Experiment: Experimental Procedures and Results," J. Air Pollut. Control Assoc., 27, No. 1 (1977).

References (Cont.)

52.   Chock, D.P., "General Motors Sulfate Dispersion Experiment: Assessment of the EPA Hiway Model," J. Air Pollut. Control Assoc., 27, No. 1 (1977).

53.   Wilson, W.E., et al., "General Motors Sulfate Dispersion Experiment: Summary of EPA Measurements," J. Air Pollut. Control Assoc., 27, No. 1 (1977).

54.   Bowman, C.T., "Kinetics of Pollutant Formation and Destruction in Combustion," Prog. Energy Combust., Science, No. 1, 33 (1975).

55.   Raine, R.R., Duggal, V.K., and Pratt, N.H., "A Comprehensive Review of Diesel Combustion Models for NO_x and Smoke Emissions," Consultation Report No. 108176, University of Southampton, Southampton, England (November 1976).

56.   Zeldovich, Y.B., Sodovnikov, P.Y., and Frank-Kamenetski, D.A., "Oxidation of Nitrogen in Combustion," Academy of Sciences of USSR, Institute of Chemical Physics, Moscow-Lenigrad (1947).

57.   Lavoie, G.A., Heywood, J.B., and Keck, J.C., "Experimental and Theoretical Study of Nitric Oxide Formation in Internal Combustion Engines," Combust. Sci. Technology, 1, 313 (1970).

58.   Baulch, D.L. Drysdale, D.D., Horne, D.B., and Lloyd, A.C., "Evaluated Kinetic Data for High Temperature Reactions," Vol. 2, CRC Press, Cleveland, Ohio (1973).

59.   Sarofin, A.G. and Pohl, J.H., "Kinetics of Nitric Oxide Formation in Premixed Laminar Flames," Fourteenth Symposium (International) on Combustion, p. 739, The Combustion Institute (1973).

60.   Homer, J.G. and Sutton, M.M., "Nitric Oxide Formation and Radical Overshoot in Premixed Hydrogen Flames," Combust. Flame, 20, 1 (1973).

61.   Bowman, C.T., "Investigation of NO Formation Kinetics in Combustion Processes: The H_2, O_2, N_2 Reaction," Combust. Sci. Tech., 3, 37 (1971)

62.   Fenimore, C.P., "Reactions of Fuel-Nitrogen in Rick Flame Gases," Combust. Flame, 26, 249 (1976).

63.   Fenimore, C.P., "Formation of Nitric Oxide From Fuel Nitrogen in Ethylene Flames," Combust. Flame, 19, 289 (1972).

64.   Lyon, R.K. and Lungwell, J.P., "Selectrive Noncatalytic Reduction of NO_x with NH_3," EPRI NO_x Control Technology Seminar, San Francisco (February 1976).

References (Cont.)

65. Begeman, C.R. and Colucci, J.M., "Polynuclear Aromatic Hydrocarbon Emissions From Automotive Engines," SAE, Paper 700469 (1970).

66. Giger, W. and Blumer, M., "Polycyclic Aromatic Hydrocarbons in the Environment: Isolation and Characterization by Chromatography, Visible, Ultraviolet, and Mass Spectroscopy," Anal. Chem., 46, 1663 (1974).

67. Greinke, R.A. and Lewis, I.C., "Development of a Gas Chromatographic - Ultraviolet Absorption Spectroscopic Method for Monitoring Petroleum Pitch Volatiles in the Environment," Anal. Chem., 47, 2151 (1975).

68. Lavoi, G.A. and Blumber, P.N., "Measurements of NO Emissions From a Stratified Charge Engine: Comparison of Theory and Experiment," Combust. Sci. Tech., 8, 25 (1973).

69. Lefebvre, A.H. (Ed), " Lean Premixed/Prevaporized Cobustion," Workshop at Lewis Research Center, Cleveland, Ohio, NASA CP-2016 (January 20-21, 1977).

70. "Aircraft Engine Emissions," Conference held at Lewis Research Center, NASA CP-2021 (May 18-19, 1977).

71. Roberts, R., Peduzzi, H., and Niedzwiecki, R.W., "Low Pollution Combustor Designs for CTOL Engines - Results of the Experimental Clean Combustor Program," AIAA Paper No. 76-762 (July 26-29, 1976).

72. Gleason, C.C. and Niedzwiecki, R.W., "Results of the NASA/General Electric Experimental Clean Combustor Program," AIAA Paper 76-763 (July 26-29, 1976).

73. Tabaczynski, R.J., "Turbulence and Turbulent Combustion in Spark Ignition Engines," Prog. Energy Comb. Sci., 2, 143 (1976).

74. Semenov, E.S., "Studies of Turbulent Gas Flow in Piston Engines," NASA Technical Transaction F-97 (1963).

75. Taylor, E.S., Personal Communication (March 1978).

76. Chigier, N.A., "The Atomization and Burning of Liquid Fuel Sprays," Prog. Energy Comb. Sci., 2, 97 (1976).

77. Samson, R., Bedeaux, D., Saxton, M.J., and Deutch, J.M., "A Sample Model of Fuel Spray Burning I: Random Sprays," Combust. Flame, 31, 215-221 (1978). "A Sample Model of Fuel Spray Burning II: Linear Droplet Streams," Combust. Flame, 31, 223 (1978).

References (Cont.)

78.   Jones, A.R., "A Review of Drop Size Measurement - The Application of
      Techniques to Dense Fuel Sprays," Prog. Energy Comb. Sci., 3, 225 (1977).

79.   Faeth, G.M., "Current Status of Droplet and Liquid Combustion," Prog.
      Energy Comb. Sci., 3, 191 (1977).

80.   Charles, R., Private Communication, 1977.

81.   "A New Approach to Variable Displacement," Automotive Ener., 85,
      30 (May 1977).

82.   Bryzik, W., "Adabatic Diesel Engine," Research/Development, (January 1978).

APPENDIX B

REPORT OF INVENTIONS

The work presented in this report is of a review nature. No invention or application for patent rights evolved from the performance of this work.

U.S. DEPARTMENT OF TRANSPORTATION
RESEARCH AND SPECIAL PROGRAMS ADMINISTRATION

TRANSPORTATION SYSTEMS CENTER
KENDALL SQUARE, CAMBRIDGE, MA. 02142

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF TRANSPORTATION
613

U.S.MAIL